

#6

C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 27th of April, 2000 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 8th day of May, 2003


Takashi KOJIMA

(Translation)

PATENT OFFICE
JAPANESE GOVERNMENT

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Applicant(s): Shin-Etsu Chemical Co., Ltd.

September 8, 2000

Commissioner,
Patent Office

Kozo OIKAWA

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[List of Documents Attached]

[Document]	Specification	1
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[Document]	Abstract	1
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[Necessity of Proof] Yes

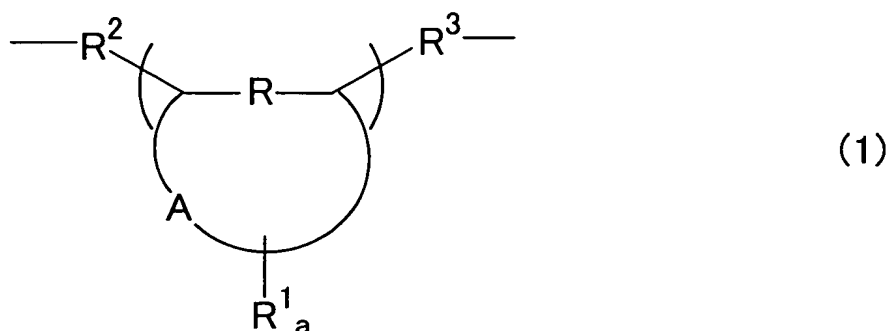
2000-127513

[SPECIFICATION]

[TITLE OF THE INVENTION] Polymer, Chemically Amplified
Resist Composition and Patterning
Process

[CLAIMS]

[Claim 1] A polymer comprising recurring units of the following general formula (1):



10 wherein A is a divalent aliphatic or alicyclic hydrocarbon group of 2 to 20 carbon atoms, R¹ is an alkyl group containing at least one fluorine atom, which may contain a hetero atom such as oxygen, nitrogen or sulfur to form an ether, ester, carbonate, alcohol, acetoxy or thioester, "a"
15 is a positive number of 1 to 3, and R, R² and R³ each are a single bond or methylene group.

[Claim 2] The polymer of claim 1 comprising the recurring units of claim 1 and recurring units containing acid labile groups.

20 [Claim 3] A chemically amplified resist composition comprising the polymer of claim 1 or 2.

[Claim 4] A chemically amplified positive resist composition comprising

- 25 (A) the polymer of claim 1 or 2,
(B) an organic solvent, and
(C) a photoacid generator.

[Claim 5] The resist composition of claim 3 or 4 further comprising a basic compound.

[Claim 6] The resist composition of claim 3, 4 or 5 further comprising a dissolution inhibitor.

[Claim 7] A process for forming a resist pattern comprising the steps of:

5 applying the resist composition of any one of claims 3 to 6 onto a substrate to form a coating,

 heat treating the coating and then exposing it to high-energy radiation having a wavelength of up to 180 nm or electron beams through a photo mask, and

10 optionally heat treating the exposed coating and developing it with a developer.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

15 This invention relates to a polymer useful as a base polymer in a chemically amplified resist composition suited for micropatterning technology, a chemically amplified resist composition, and a patterning process using the resist composition.

20 [0002]

[Prior Art and Problem to be Solved by the Invention]

 In the drive for higher integration and operating speeds in LSI devices, the pattern rule is made drastically finer. The rapid advance toward finer pattern rules is
25 grounded on the development of a projection lens with an increased NA, a resist material with improved performance, and exposure light of a shorter wavelength. In particular, the change-over from i-line (365 nm) to shorter wavelength KrF laser (248 nm) brought about a significant innovation,
30 enabling mass-scale production of 0.18 micron rule devices. To the demand for a resist material with a higher resolution and sensitivity, acid-catalyzed chemical amplification positive working resist materials are effective as disclosed in USP 4,491,628 and USP 5,310,619 (JP-B 2-27660 and JP-A
35 63-27829). They now become predominant resist materials especially adapted for deep UV lithography.

[0003]

Resist materials adapted for KrF excimer lasers enjoyed early use on the 0.3 micron process, went through the 0.25 micron rule, and currently entered the mass
5 production phase on the 0.18 micron rule. Engineers have started investigation on the 0.15 micron rule, with the trend toward a finer pattern rule being accelerated. A wavelength change-over from KrF to shorter wavelength ArF laser (193 nm) is expected to enable miniaturization of the
10 design rule to 0.13 μm or less. Since conventionally used novolak resins and polyvinylphenol resins have very strong absorption in proximity to 193 nm, they cannot be used as the base resin for resists. To ensure transparency and dry etching resistance, some engineers investigated acrylic and
15 alicyclic (typically cycloolefin) resins as disclosed in JP-A 9-73173, JP-A 10-10739, JP-A 9-230595 and WO 97/33198. With respect to F_2 excimer laser (157 nm) which is expected to enable further miniaturization to 0.10 μm or less, more difficulty arises in insuring transparency because it was
20 found that acrylic resins are not transmissive to light at all and those cycloolefin resins having carbonyl bonds have strong absorption. It was also found that polyvinylphenol is somewhat improved in transmittance in proximity to 160 nm, but far below the practical level, and reducing carbonyl
25 and carbon-to-carbon double bonds is essential for insuring a transmittance. However, cyclic structures and carbon-to-carbon double bonds greatly contribute to an improvement in dry etching resistance. A polymer for use with an ArF excimer laser, in which a benzene ring is
30 excluded and instead, an alicyclic structure is introduced for improving etching resistance, is difficult to provide transparency since it acquires solubility by relying on carboxylic acid.

[0004]

35 The present invention has been done in view of the above circumstances. An object of the invention is to provide a novel polymer useful as the base polymer in

chemical amplification resist compositions, a chemical amplification resist composition comprising the polymer, and a patterning process using the same, which resist composition has a high transmittance to vacuum ultraviolet radiation of up to 300 nm, especially an F₂ beam (157 nm), Kr₂ beam (146 nm), KrAr beam (134 nm) and Ar₂ beam (126 nm), as well as improved negative conversion-preventing effect and dry etching resistance.

[0005]

10 [Means for Solving the Problem and Embodiment of the Invention]

In order to attain the above object, the inventors have earnestly studied. As a result, it has been found that using a cycloolefin polymer having fluorinated alkyl groups as the base polymer, a resist composition featuring transparency and alkali solubility is obtained.

[0006]

That is, the use of a fluorine-substituted polymer was found effective as a means for improving transparency.

20 Making a study to improve the transparency of an acrylic polymer used in ArF resist compositions, the inventors proposed the use of an acrylic derivative having a fluorine-substituted backbone.

[0007]

25 In most cases, dry etching resistance is conventionally discussed in conjunction with the selection ratio of etching. As described in many reports, for example, J. Photopolymer Sci. and Technol., Vol. 5, No. 3 (1992), p. 439, J. Electrochem. Soc.: Solid-State Sci. and Technol., Vol. 130, No. 1, January 1983, p. 143, and SPIE, Vol. 2724, p. 365 (1996), engineers attempted to express the dry etching selection ratio of a single layer resist using various parameters. Typical are Onishi parameter and ring parameter.

35 [0008]

It was recently reported in SPIE, Vol. 3678, p. 1209 (1999) that micro-roughness develops on the resist surface

after dry etching and is transferred after substrate processing and resist removal. Making extensive studies, the inventor found that the development of roughness after etching occurs when dry etching of SiO_2 is carried out with a fluorocarbon gas such as CF_4 , CHF_3 , C_2F_6 , C_3F_8 or C_4F_{10} and that roughness increases under the high throughput conditions where the RF power is increased for high etching selection ratio, that is, fast etching of oxide film. It was further found that roughness largely differs depending on the type of polymer used in ArF single layer resist. A noticeable roughness develops with acrylic polymers. In contrast, roughness declines with cycloolefin polymers such as norbornene homopolymers and alternating copolymers of norbornene with maleic anhydride. In particular, norbornene homopolymers give small values of roughness even compared with polyhydroxystyrene for KrF. Herein, acrylic polymers with pendant adamantane exhibit a satisfactory value of etching speed, that is, selection ratio, fully comparable to cycloolefin polymers. When high selectivity etching was effected in an etching speed ratio of at least 3 between oxide film and resist, the surface roughness Rms of the etched surface as measured by atomic force microscopy (AFM) was more than 15 nm for acrylic polymers and less than 3 nm for cycloolefin polymers. These results indicate that the selection ratio of etching does not necessarily coincide with the roughness after etching.

[0009]

As described above, the introduction of fluorine is effective as a method of improving transparency at about 157 nm. Especially, it has been found that the effect of introducing a fluorinated alkyl is high. So, the inventors have tried the introduction of a fluorinated alkyl to a cycloolefin ring having an excellent dry etching resistance.

[0010]

It is pointed out that what becomes a problem as a result of wavelength reduction is a lowering of transparency, and in the case of a positive resist material,

a negative working phenomenon that the exposed areas become insoluble as the dose of exposure is increased. Those portions which have turned negative are insoluble not only in alkali developers, but also in organic solvents such as acetone. This indicates that gel forms as a result of crosslinking of molecules together. Radical generation is probably one cause of crosslinking. As a result of wavelength reduction, the exposure energy is increased so that even C-C bonds and C-H bonds may be excited in the case of F₂ exposure (157 nm). As a result of excitation, radicals are generated with a possibility that molecules are bonded together. For polymers having an alicyclic structure for use in ArF exposure, for example, polynorbornene, an outstanding negative working phenomenon was observed. It is believed that these polymers have a structure susceptible to crosslinking since the alicyclic group has many C-H bonds at the bridgehead. On the other hand, it is well known that α -methylstyrene and derivatives thereof are effective for preventing crosslinking. Alpha-methylstyrene can mitigate the negative working phenomenon, but fail to completely eliminate the phenomenon. Moreover, since oxygen absorption is considerable in the VUV region, exposure is effected under the conditions that oxygen is purged, with an inert gas such as nitrogen or argon, to an oxygen concentration of 1 ppm or lower. Since oxygen is an effective radical trapping agent, this means that the radicals generated have a long lifetime and more crosslinking takes place.

[0011]

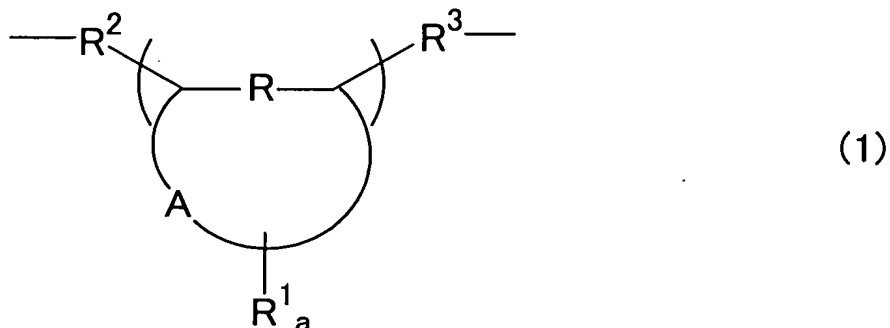
A remarkable negative working phenomenon has been observed in a resist composition especially containing a polyhydroxystyrene base polymer among resist polymers. On the other hand, it has been found that a resist composition containing an acrylate base polymer shows little negative working phenomenon. Moreover, it has also been found that a resist composition containing an alternating copolymer of norbornene and maleic anhydride as a base polymer shows little negative working phenomenon.

[0012]

Accordingly, the present invention provides the following polymer, a chemically amplified resist composition, and a pattern forming process.

5 Claim 1:

A polymer comprising recurring units of the following general formula (1):



10 wherein A is a divalent aliphatic or alicyclic hydrocarbon group of 2 to 20 carbon atoms, R¹ is an alkyl group containing at least one fluorine atom, which may contain a hetero atom such as oxygen, nitrogen or sulfur to form an ether, ester, carbonate, alcohol, acetoxy or thioester, "a" is a positive number of 1 to 3, and R, R² and R³ each are a single bond or methylene group.

15 Claim 2:

The polymer of claim 1 comprising the recurring units of claim 1 and recurring units containing acid labile groups.

20 Claim 3:

A chemically amplified resist composition comprising the polymer of claim 1 or 2.

Claim 4:

25 A chemically amplified positive resist composition comprising

- (A) the polymer of claim 1 or 2,
- (B) an organic solvent, and
- (C) a photoacid generator.

Claim 5:

The resist composition of claim 3 or 4 further comprising a basic compound.

Claim 6:

5 The resist composition of claim 3, 4 or 5 further comprising a dissolution inhibitor.

Claim 7:

A process for forming a resist pattern comprising the steps of:

10 applying the resist composition of any one of claims 3 to 6 onto a substrate to form a coating,

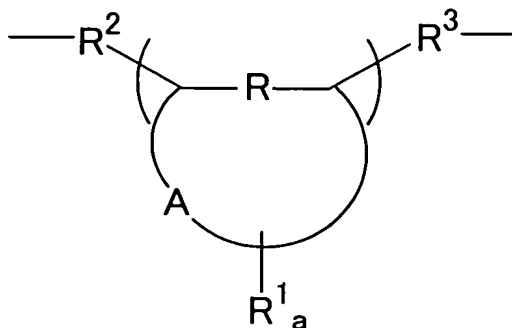
heat treating the coating and then exposing it to high-energy radiation having a wavelength of up to 180 nm or electron beams through a photo mask, and

15 optionally heat treating the exposed coating and developing it with a developer.

[0013]

The following is the detailed description of the invention.

20 The polymer of the present invention comprises recurring units of the following general formula (1).

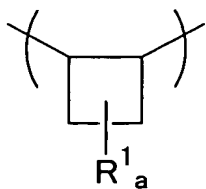


Herein A is a divalent aliphatic or alicyclic hydrocarbon group of 2 to 20 carbon atoms, R¹ is an alkyl group
25 containing at least one fluorine atom, which may contain a hetero atom such as oxygen, nitrogen or sulfur to form an ether, ester, carbonate, alcohol, acetoxy or thioester, "a" is a positive number of 1 to 3, and R, R² and R³ each are a single bond or methylene group.

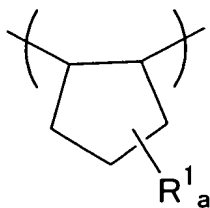
[0014]

Preferred among the polymers of formula (1) are those polymers of the following formulas (2)-1 to (2)-9.

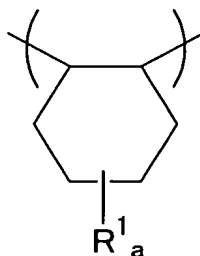
[0015]



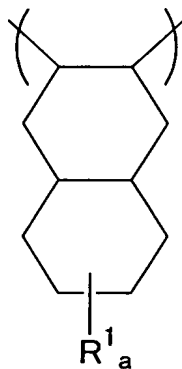
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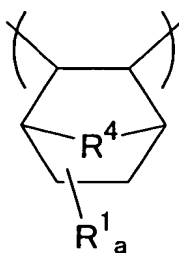
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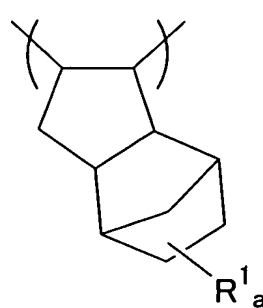
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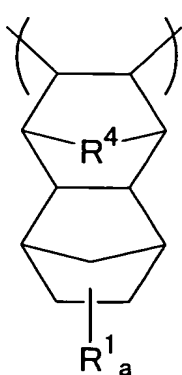
(2)-4



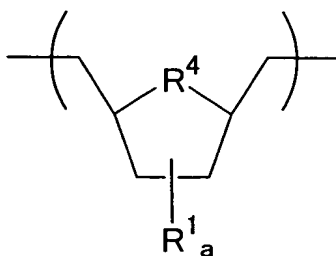
(2)-5



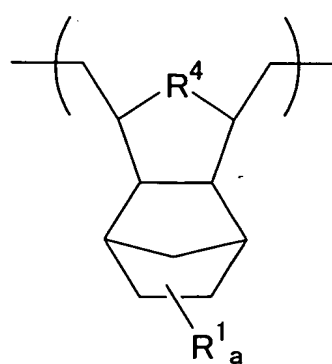
(2)-6



(2)-7



(2)-8



(2)-9

Herein R^4 is a methylene group, oxygen atom, NH group or sulfur atom.

[0016]

Examples of the fluorine-containing substituents represented by R^1 include those of the following formulas (3)-1 to (3)-9.

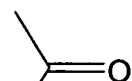
5 [0017]



(3)-1



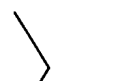
(3)-2



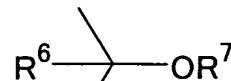
(3)-3



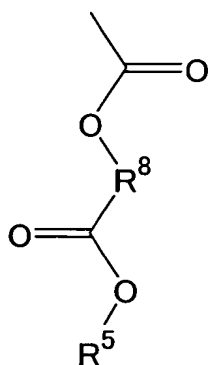
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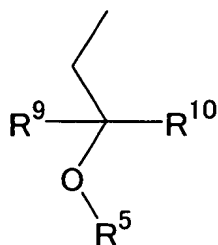
(3)-5



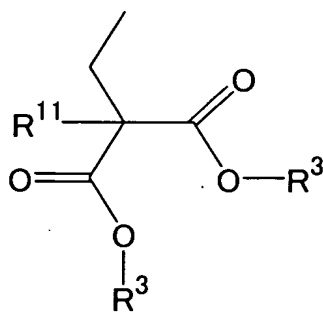
(3)-6



(3)-7



(3)-8



(3)-9

[0018]

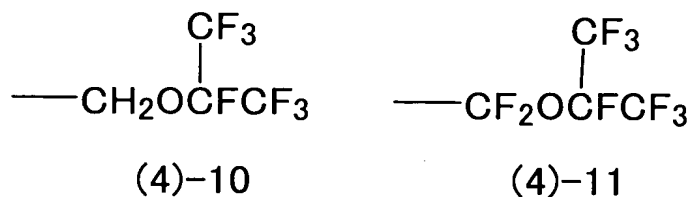
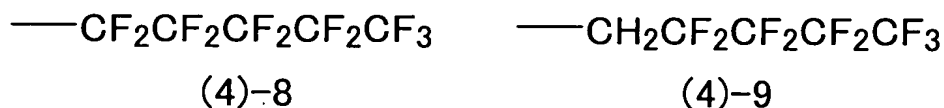
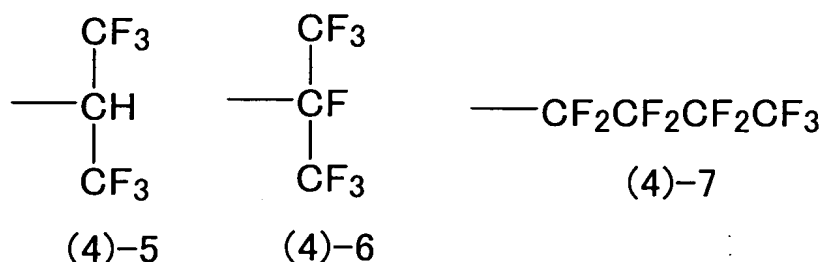
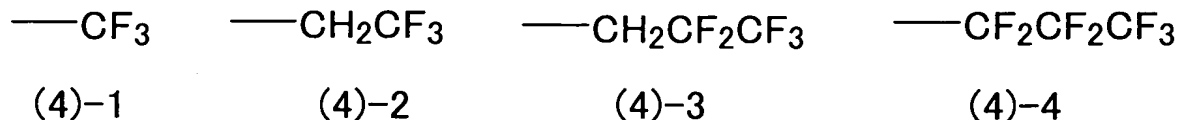
Herein, R^5 is a fluorinated alkyl group which may contain an ether or ester bond; R^6 and R^{11} each are hydrogen or a straight alkyl group of 1 to 10 carbon atoms, R^7 is hydrogen, a straight alkyl group of 1 to 10 carbon atoms, or $-\text{C}=\text{O}-\text{R}^{12}$ wherein R^{12} is hydrogen or a straight alkyl group of 1 to 10 carbon atoms; R^8 is an alkylene group of 1 to 10 carbon atoms; either one or both of R^9 and R^{10} are alkyl groups of 1 to 5 carbon atoms having at least one fluorine atom substituted thereon.

[0019]

Preferably, R⁵ is a straight, branched or cyclic alkyl group of 1 to 20 carbon atoms which contains at least one fluorine atom and which may contain an ether or ester bond.

5 Illustrative examples are substituents of the following formulas (4)-1 to (4)-11.

[0020]



[0021]

10 In a preferred embodiment, the inventive polymer comprises recurring units containing acid labile groups in addition to the above units.

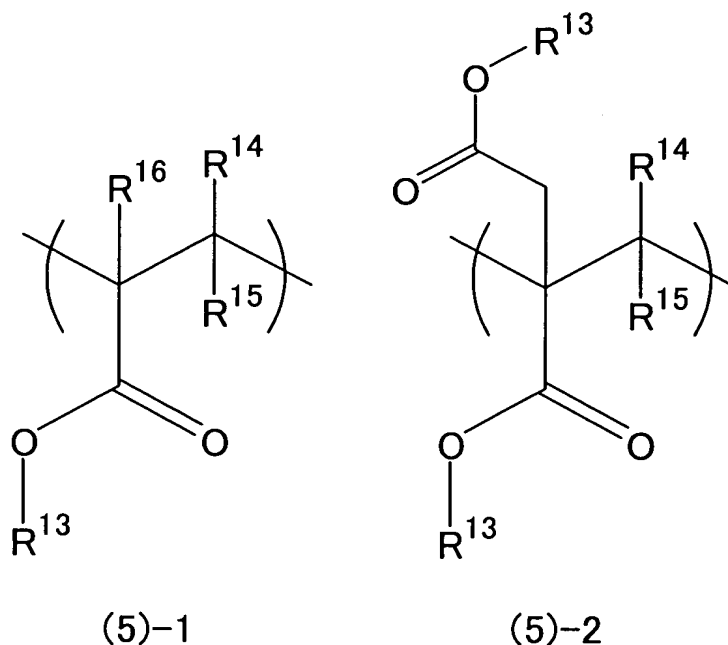
[0022]

The recurring units containing acid labile groups are desirably those units having a carbon-to-carbon double bond and capable of copolymerizing with the recurring units of formula (1), for example, units of (meth)acrylic derivatives, styrene derivatives, norbornene derivatives, tricyclododecene derivatives, tetracyclododecene derivatives, maleimide derivatives, and vinyl alcohol derivatives.

[0023]

The (meth)acrylic derivatives are exemplified by the following formulas (5)-1 and (5)-2.

[0024]



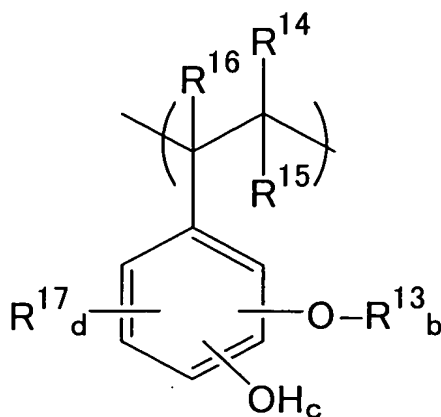
[0025]

In formulas (5)-1 and (5)-2, R^{13} is an acid labile group, each of R^{14} , R^{15} and R^{16} is a hydrogen atom, fluorine atom, or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, which may be substituted with fluorine.

[0026]

The styrene derivatives are exemplified by the following formula (6).

[0027]



(6)

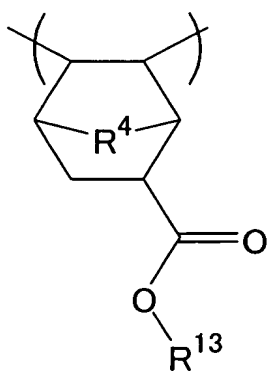
[0028]

In formula (6), R¹³, R¹⁴, R¹⁵ and R¹⁶ are as defined above, R¹⁷ is a hydrogen atom, fluorine atom, or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, which may be substituted with fluorine, b is a positive number of 1 to 5, c and d each are 0 or a positive number of 1 to 4.

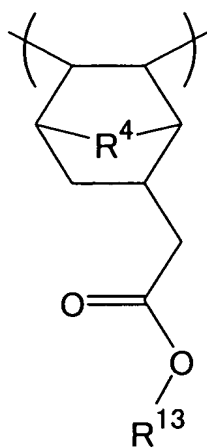
[0029]

The norbornene derivatives are exemplified by the following formulas (7)-1 to (7)-7.

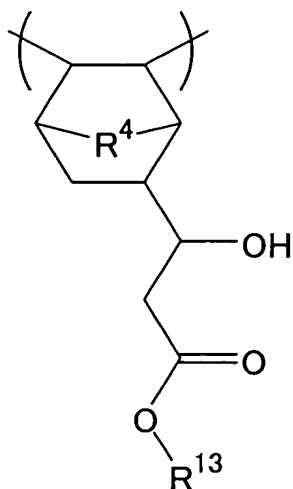
[0030]



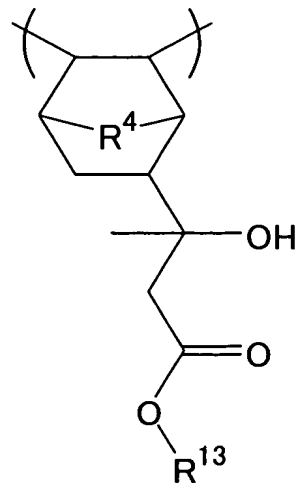
(7)-1



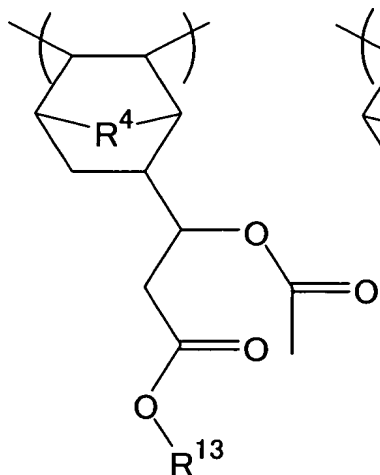
(7)-2



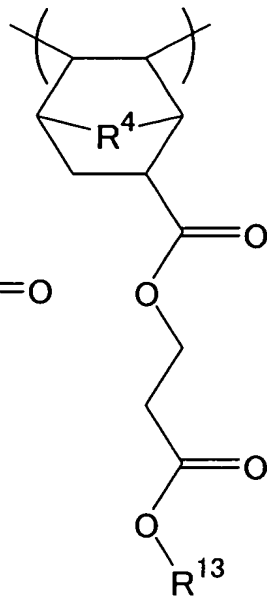
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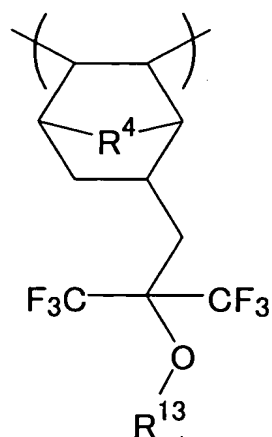
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(7)-5



(7)-6



(7)-7

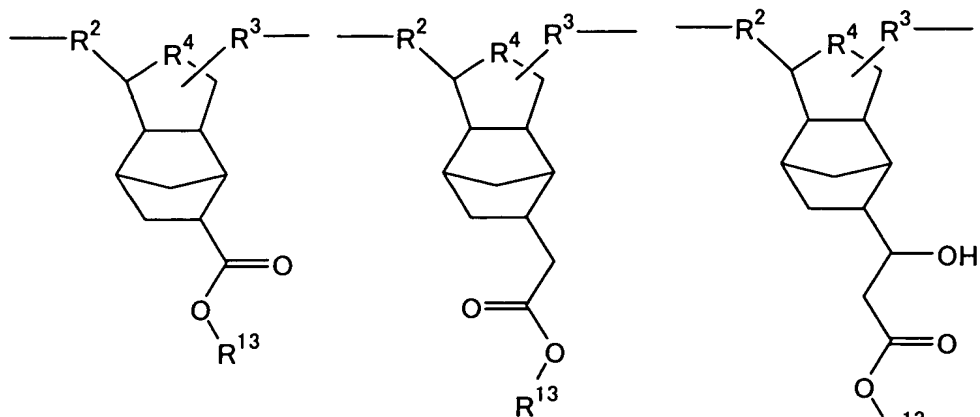
Herein, R^4 and R^{13} are as defined above.

[0031]

5

The tricyclodecene derivatives are exemplified by the following formulas (8)-1 to (8)-7.

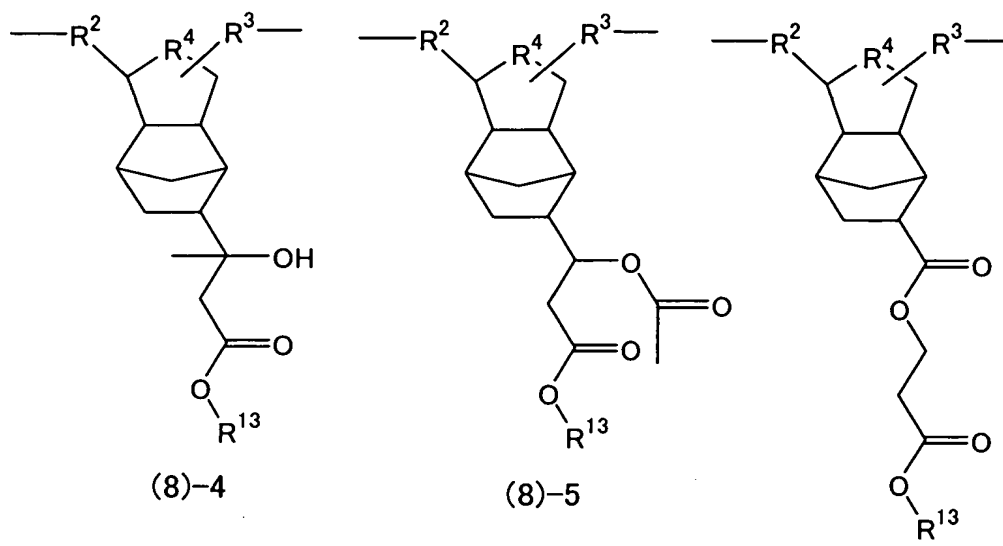
[0032]



(8)-1

(8)-2

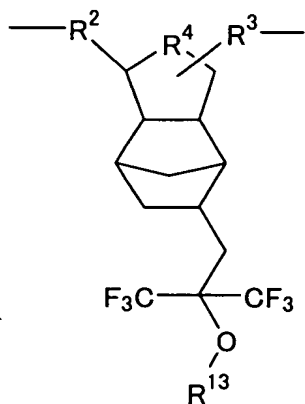
(8)-3



(8)-4

(8)-5

(8)-6



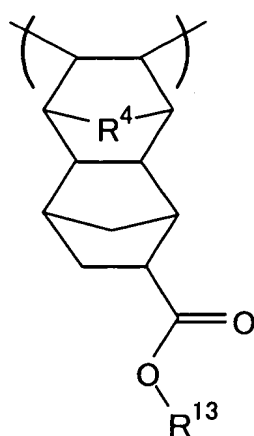
(8)-7

Herein, R^2 , R^3 , R^4 and R^{13} are as defined above.

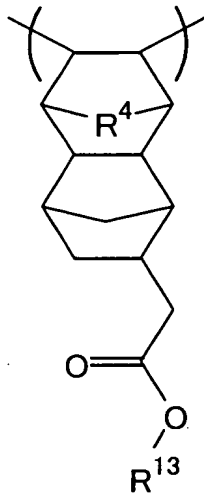
[0033]

The tetracyclododecene derivatives are exemplified by the following formulas (9)-1 to (9)-7.

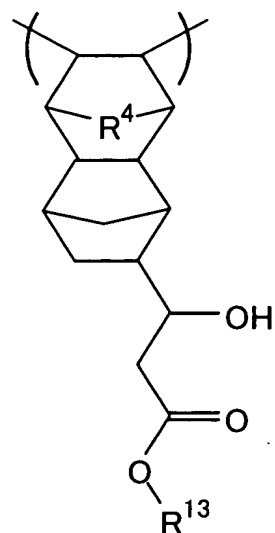
[0034]



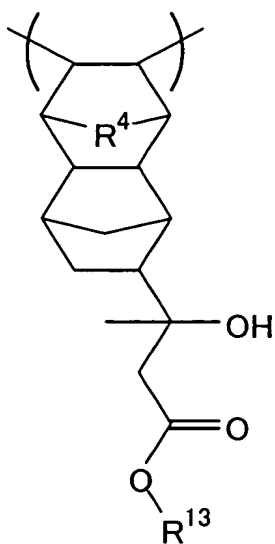
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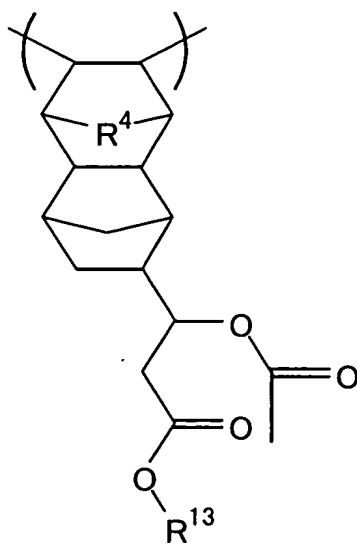
(9)-2



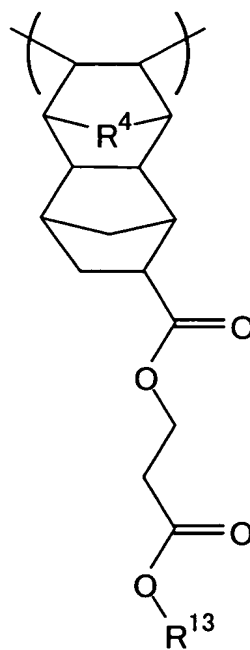
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(9)-4

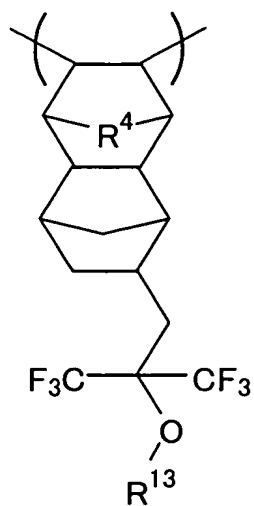


(9)-5



(9)-6

[0035]



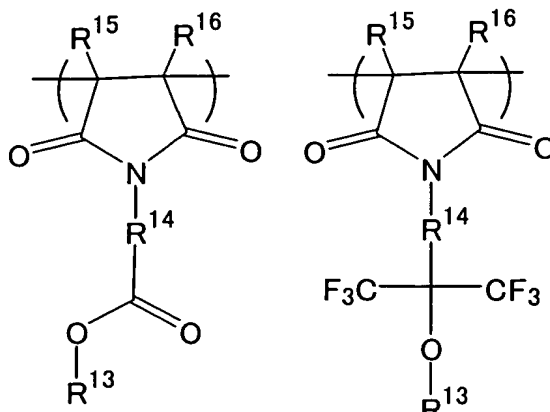
(9)-7

Herein, R^4 and R^{13} are as defined above.

[0036]

5 The maleimide derivatives are exemplified by the following formulas (10)-1 and (10)-2.

[0037]



(10)-1

(10)-2

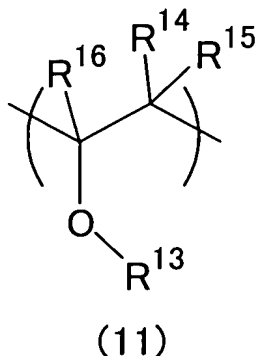
[0038]

10 Herein, R^{13} is as defined above, R^{14} is a single bond or an alkylene group of 1 to 10 carbon atoms, R^{15} and R^{16} each are hydrogen, fluorine, methyl or trifluoromethyl.

[0039]

The vinyl alcohol derivatives are exemplified by the following formula (11).

[0040]



5

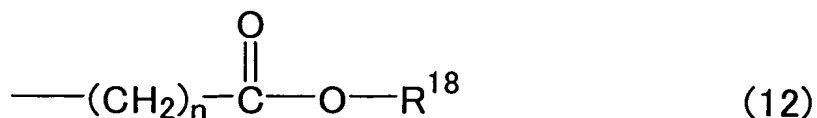
Herein, R^{13} , R^{14} , R^{15} and R^{16} are as defined above.

[0041]

The acid labile group represented by R^{13} is selected from a variety of such groups, preferably from among the groups of the following formulas (12) and (13), tertiary alkyl groups with 4 to 40 carbon atoms of the following formula (14), trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, and oxoalkyl groups of 4 to 20 carbon atoms.

15

[0042]



[0043]

In formulas (12) and (13), R^{18} and R^{21} each are a straight, branched or cyclic alkyl group of 1 to 20 carbon atoms, which may contain a hetero atom such as oxygen, sulfur, nitrogen or fluorine; R^{19} and R^{20} each are hydrogen, a straight, branched or cyclic alkyl group of 1 to 20 carbon atoms, which may contain a hetero atom such as oxygen, sulfur, nitrogen or fluorine; and n is 0 or an integer of 1 to 10. A pair of R^{19} and R^{20} , a pair of R^{19} and R^{21} or a pair of R^{20} and R^{21} may bond together to form a ring.

[0044]

Preferably, R^{18} to R^{21} are as illustrated below.

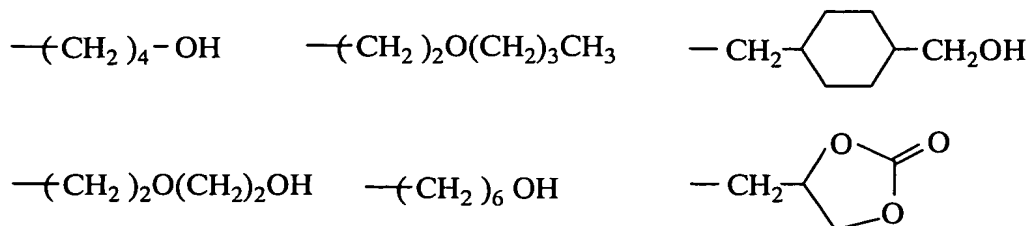
R^{18} is a tertiary alkyl group of 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, a trialkylsilyl group whose alkyl groups each have 1 to 6 carbon atoms, an oxoalkyl group of 4 to 20 carbon atoms or a group of formula (14). Exemplary tertiary alkyl groups are tert-butyl, tert-amyl, 1,1-diethylpropyl, 1-ethylcyclopentyl, 1-butylcyclopentyl, 1-ethylcyclohexyl, 1-butylcyclohexyl, 1-ethyl-2-cyclopentenyl, 1-ethyl-2-cyclohexenyl, and 2-methyl-2-adamantyl. Exemplary trialkylsilyl groups are trimethylsilyl, triethylsilyl, and dimethyl-tert-butylsilyl. Exemplary oxoalkyl groups are 3-oxocyclohexyl, 4-methyl-2-oxooxan-4-yl, and 5-methyl-5-oxooxolan-4-yl. Letter "a" is an integer of 0 to 6.

[0045]

R^{19} and R^{20} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, cyclopentyl, cyclohexyl, 2-ethylhexyl and n-octyl. R^{21} is a monovalent hydrocarbon group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, which may have a hetero atom such as oxygen atom, for example, straight, branched or cyclic alkyl groups, and such groups in which some hydrogen atoms are replaced by hydroxyl, alkoxy, oxo, amino or

alkylamino groups. Illustrative examples of the substituted alkyl groups are given below.

[0046]



5 [0047]

A pair of R^{19} and R^{20} , a pair of R^{19} and R^{21} , or a pair of R^{20} and R^{21} , taken together, may form a ring. Each of R^{19} , R^{20} and R^{21} is a straight or branched alkylene group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, when they

10 form a ring.

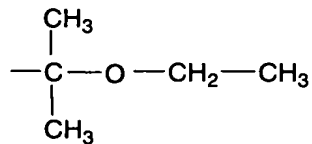
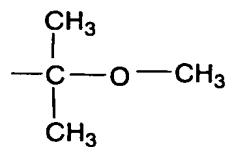
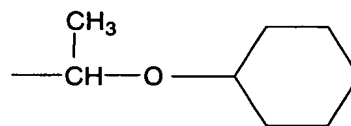
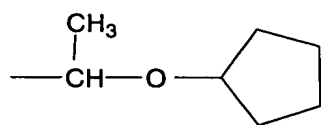
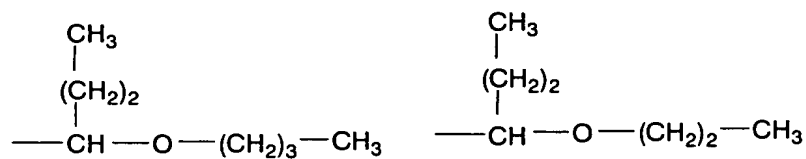
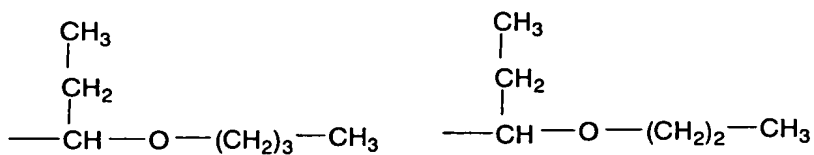
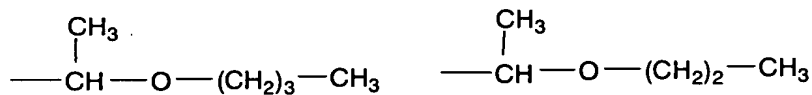
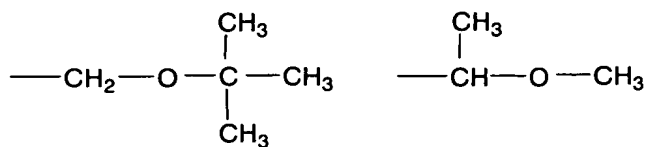
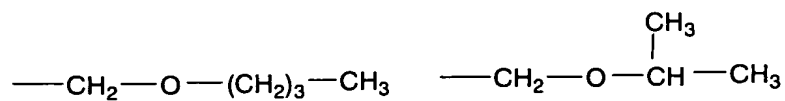
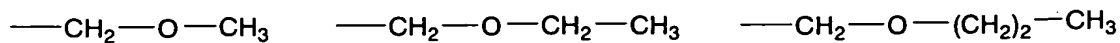
[0048]

Illustrative examples of the acid labile groups of formula (12) include tert-butoxycarbonyl, tert-butoxycarbonylmethyl, tert-amyloxycarbonyl, tert-amyloxycarbonylmethyl, 1,1-diethylpropyloxycarbonyl, 1,1-diethylpropyloxycarbonylmethyl, 1-ethylcyclopentyloxycarbonyl, 1-ethylcyclopentyloxycarbonylmethyl, 1-ethyl-2-cyclopentenylloxycarbonyl, 1-ethyl-2-cyclopentenylloxycarbonylmethyl, 1-ethoxyethoxycarbonylmethyl, 2-tetrahydropyranyloxycarbonylmethyl, and 2-tetrahydrofuranyloxycarbonylmethyl.

[0049]

25 Of the acid labile groups of formula (13), illustrative examples of the straight or branched groups are given below.

[0050]



[0051]

Of the acid labile groups of formula (13), illustrative examples of the cyclic groups include tetrahydrofuran-2-yl, 2-methyltetrahydrofuran-2-yl, tetrahydropyran-2-yl and 2-methyltetrahydropyran-2-yl. Preferred among the groups of formula (13) are ethoxyethyl, butoxyethyl and ethoxypropyl.

[0052]

In formula (14), R^{22} , R^{23} and R^{24} are independently monovalent hydrocarbon groups, for example, straight, branched or cyclic alkyl groups of 1 to 20 carbon atoms, which may contain a hetero atom such as oxygen, sulfur, nitrogen or fluorine. A pair of R^{22} and R^{23} , a pair of R^{22} and R^{24} , or a pair of R^{23} and R^{24} , taken together, may form a ring.

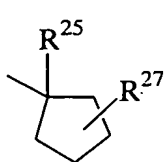
[0053]

Examples of the tertiary alkyl group represented by formula (14) include tert-butyl, triethylcarbyl, 1-ethylnorbornyl, 1-methylcyclohexyl, 1-ethylcyclopentyl, 2-(2-methyl)adamantyl, 2-(2-ethyl)adamantyl, and tert-amyl.

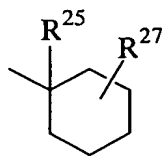
[0054]

Other illustrative examples of the tertiary alkyl group are given below as formulae (15-1) through (15-16).

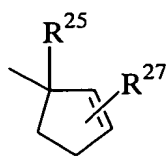
[0055]



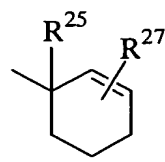
(15-1)



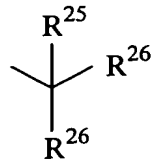
(15-2)



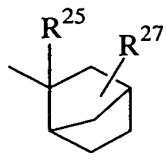
(15-3)



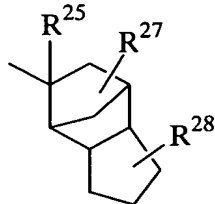
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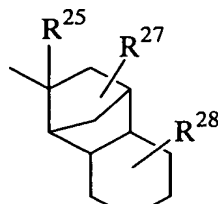
(15-5)



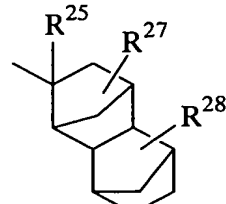
(15-6)



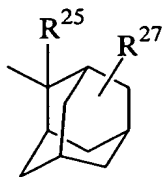
(15-7)



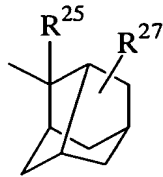
(15-8)



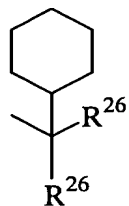
(15-9)



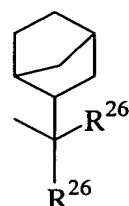
(15-10)



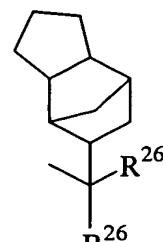
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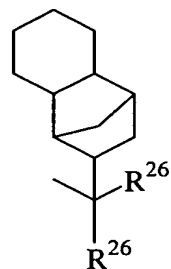
(15-12)



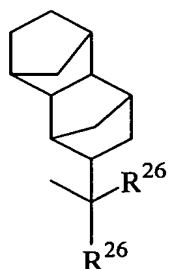
(15-13)



(15-14)



(15-15)



(15-16)

[0056]

Herein, each of R^{25} and R^{26} is a straight, branched or
 5 cyclic alkyl group of 1 to 6 carbon atoms, for example,
 methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl,
 n-pentyl, n-hexyl, cyclopropyl or cyclopropylmethyl. R^{27} is
 hydrogen, a monovalent hydrocarbon group of 1 to 6 carbon

atoms which may contain a hetero atom, or a monovalent hydrocarbon group of 1 to 6 carbon atoms, typically alkyl, which may be separated by a hetero atom. The hetero atom is an oxygen, sulfur or nitrogen atom, which is contained or
5 intervenes in the form of -OH, -OR, -O-, -S-, -S(=O)-, -NH₂, -NHR, -NR₂, -NH-, or -NR- wherein R is an alkyl group of 1 to 20 carbon atoms, and especially 1 to 16 carbon atoms.

[0057]

R²⁸ is hydrogen or an alkyl, hydroxyalkyl, alkoxy or
10 alkoxyalkyl group of 1 to 20 carbon atoms, especially 1 to 16 carbon atoms, which may be straight, branched or cyclic. Illustrative examples include methyl, hydroxymethyl, ethyl, hydroxyethyl, propyl, isopropyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, methoxy, methoxymethoxy, ethoxy, and
15 tert-butoxy.

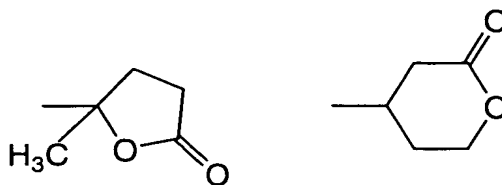
[0058]

Of the acid labile group represented by R¹³, the trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms include trimethylsilyl, triethylsilyl, and
20 tert-butyldimethylsilyl.

[0059]

The oxoalkyl groups of 4 to 20 carbon atoms include 3-oxocyclohexyl and groups of the following formulae.

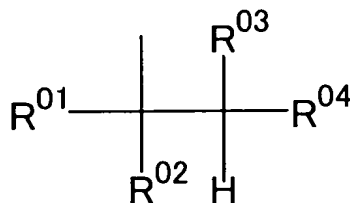
[0060]



25 [0061]

Also included are fluorine-containing acid labile groups of the following general formula (16).

[0062]



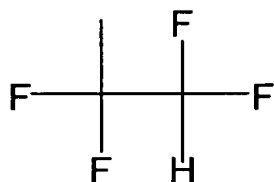
(16)

Herein, each of R^{01} , R^{02} , R^{03} , and R^{04} is a hydrogen atom, a fluorine atom or an unsubstituted or fluorinated, straight, branched or cyclic alkyl group of 1 to 20 carbon atoms.

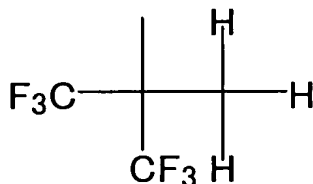
5 [0063]

More illustratively, the groups are shown by the following formulas (16)-1 to (16)-3.

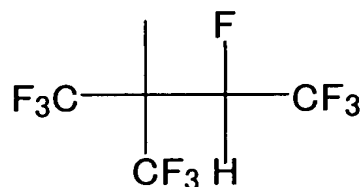
[0064]



(16)-1



(16)-2

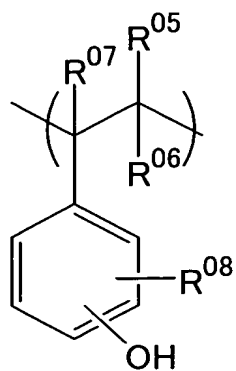


(16)-3

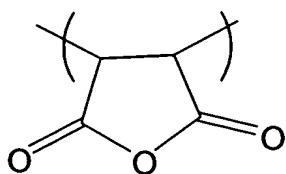
10 [0065]

When copolymers comprising units of formula (1) and acid labile group-containing units are prepared by polymerizing the corresponding monomers, there can be added an additional monomer, specifically a monomer having a substituent for improving adhesion, a monomer for improving dry etching resistance, and/or a (meth)acrylate monomer. The adhesion-improving monomer used herein is one containing a hydrophilic substituent such as a phenol, acid anhydride, ester (lactone), carbonate, alcohol, carboxylic acid, carboxylic amide, sulfonic amide or ketone group, for example, monomers of the following formulas (17)-1 to (17)-29.

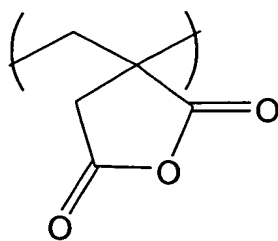
[0066]



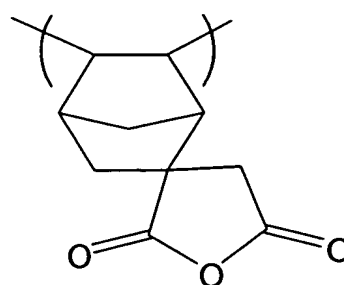
(17)-1



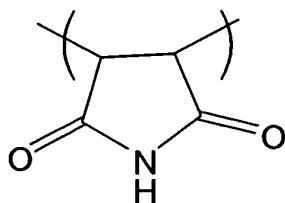
(17)-2



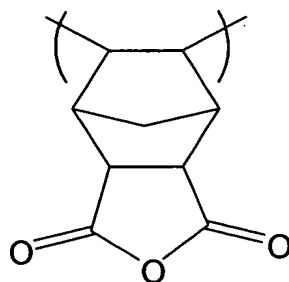
(17)-3



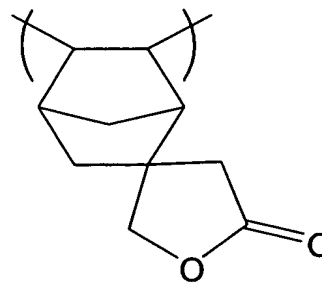
(17)-4



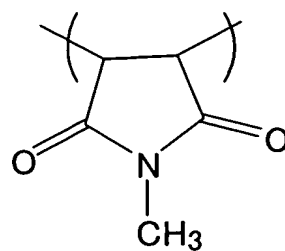
(17)-5



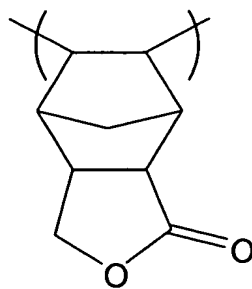
(17)-6



(17)-7

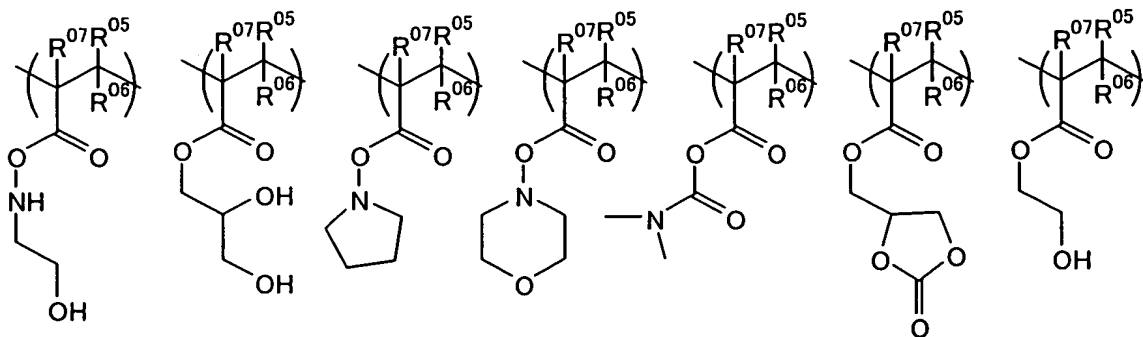


(17)-8



(17)-9

[0067]



(17)-10

(17)-11

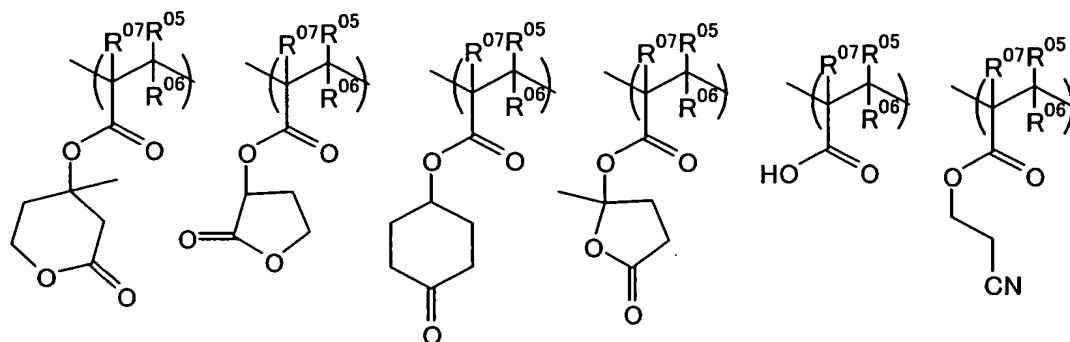
(17)-12

(17)-13

(17)-14

(17)-15

(17)-16



(17)-17

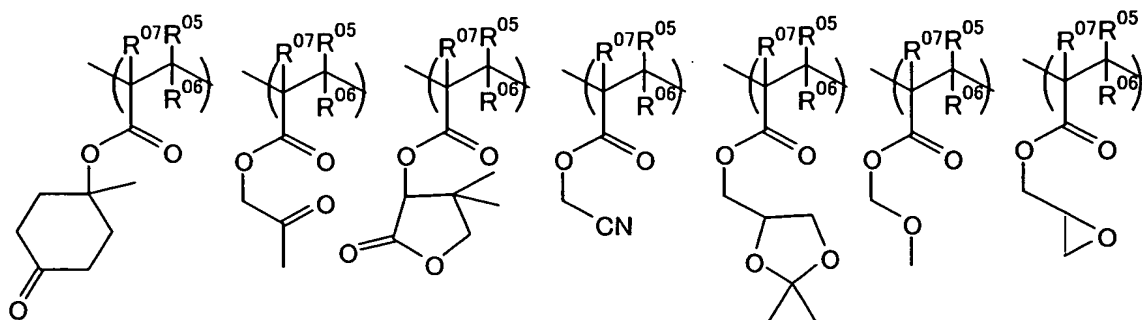
(17)-18

(17)-19

(17)-20

(17)-21

(17)-22



(17)-23

(17)-24

(17)-25

(17)-26

(17)-27

(17)-28

(17)-29

[0068]

Herein, each of R^{05} , R^{06} , R^{07} , and R^{08} is a hydrogen atom,
 5 a fluorine atom or an unsubstituted or fluorinated,
 straight, branched or cyclic alkyl group of 1 to 20 carbon
 atoms.

[0069]

The polymer or high molecular weight compound is generally prepared by mixing a polymerizable monomer corresponding to the units of formula (1) and preferably, a monomer corresponding to the acid labile group-containing units, and an optional monomer corresponding to units of formulas (17)-1 to (17)-29 with a solvent, adding a catalyst thereto, and effecting polymerization reaction while heating or cooling the system if necessary. The polymerization reaction depends on the type of initiator or catalyst, trigger means (including light, heat, radiation and plasma), and polymerization conditions (including temperature, pressure, concentration, solvent, and additives). Commonly used for the polymerization of the monomers are radical polymerization of triggering polymerization with radicals of α, α' -azobisisobutyronitrile (AIBN) or the like, ion (anion) polymerization using catalysts such as alkyl lithium, and ring-opening polymerization using metal catalysts. Such polymerization may be effected in a conventional manner.

20 [0070]

The polymer of the invention preferably has a weight average molecular weight of 1,000 to 1,000,000, and especially 2,000 to 100,000.

[0071]

25 The polymer of the invention is useful in resist compositions, and especially chemical amplification type positive resist compositions.

[0072]

Accordingly, the present invention provides a chemical amplification positive resist composition comprising
30 (A) the polymer defined above as a base resin,
(B) an organic solvent, and
(C) a photoacid generator.

[0073]

35 In this case, the resist composition may further contain

- (D) a basic compound and
- (E) a dissolution inhibitor.

[0074]

The organic solvent used as component (B) in the invention may be any organic solvent in which the photoacid generator, base resin, dissolution inhibitor, and other components are soluble. Illustrative, non-limiting, examples of the organic solvent include ketones such as cyclohexanone and methyl-2-n-amylketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; and esters such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate.

Also useful are fluorinated organic solvents. Examples include 2-fluoroanisole, 3-fluoroanisole, 4-fluoroanisole, 2,3-difluoroanisole, 2,4-difluoroanisole, 2,5-difluoroanisole, 5,8-difluoro-1,4-benzodioxane, 2,3-difluorobenzyl alcohol, 1,3-difluoro-2-propanol, 2',4'-difluoropropiophenone, 2,4-difluorotoluene, trifluoroacetaldehyde ethyl hemiacetal, trifluoroacetamide, trifluoroethanol, 2,2,2-trifluoroethyl butyrate, ethyl heptafluorobutyrate, ethyl heptafluorobutylacetate, ethyl hexafluoroglutaricmethyl, ethyl 3-hydroxy-4,4,4-trifluorobutyrate, ethyl 2-methyl-4,4,4-trifluoroacetoacetate, ethyl pentafluorobenzoate, ethyl pentafluoropropionate, ethyl pentafluoropropynylacetate, ethyl perfluorooctanoate, ethyl 4,4,4-trifluoroacetoacetate, ethyl 4,4,4-trifluorobutyrate, ethyl 4,4,4-trifluorocrotonate, ethyl trifluorosulfonate, ethyl 3-(trifluoromethyl)butyrate, ethyl trifluoropyruvate,

S-ethyl trifluoroacetate, fluorocyclohexane,
2,2,3,3,4,4,4-heptafluoro-1-butanol,
1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione,
1,1,1,3,5,5,5-heptafluoropentane-2,4-dione,
5 3,3,4,4,5,5,5-heptafluoro-2-pentanol,
3,3,4,4,5,5,5-heptafluoro-2-pentanone, isopropyl
4,4,4-trifluoroacetoacetate, methyl perfluorodecanoate,
methyl perfluoro(2-methyl-3-oxahexanoate), methyl
perfluorononanoate, methyl perfluorooctanoate, methyl
10 2,3,3,3-tetrafluoropropionate, methyl trifluoroacetoacetate,
1,1,1,2,2,6,6,6-octafluoro-2,4-hexanedione,
2,2,3,3,4,4,5,5-octafluoro-1-pentanol,
1H,1H,2H,2H-perfluoro-1-decanol, perfluoro-2,5-dimethyl-3,6-
dioxane anionic acid methyl ester, 2H-perfluoro-5-methyl-
15 3,6-dioxanonane, 1H,1H,2H,3H,3H-perfluorononane-1,2-diol,
1H,1H,9H-perfluoro-1-nonanol, 1H,1H-perfluorooctanol,
1H,1H,2H,2H-perfluorooctanol, 2H-perfluoro-5,8,11,14-
tetramethyl-3,6,9,12,15-pentaoxaoctadecane,
perfluorotributylamine, perfluorotrihexylamine, methyl
20 perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate,
perfluorotripentylamine, perfluorotripropylamine,
1H,1H,2H,3H,3H-perfluoroundecane-1,2-diol,
trifluorobutanol-1,1,1-trifluoro-5-methyl-2,4-hexanedione,
1,1,1-trifluoro-2-propanol, 3,3,3-trifluoro-1-propanol,
25 1,1,1-trifluoro-2-propyl acetate,
perfluorobutyltetrahydrofuran,
perfluoro(butyltetrahydrofuran), perfluorodecalin,
perfluoro(1,2-dimethylcyclohexane),
perfluoro(1,3-dimethylcyclohexane), propylene glycol
30 trifluoromethyl ether acetate, propylene glycol methyl ether
trifluoromethyl acetate, butyl trifluoromethylacetate,
methyl 3-trifluoromethoxypropionate, perfluorocyclohexanone,
propylene glycol trifluoromethyl ether, butyl
trifluoroacetate, and 1,1,1-trifluoro-5,5-dimethyl-2,4-
35 hexanedione. These solvents may be used alone or in
combinations of two or more thereof.

[0075]

Of the above organic solvents, preferred are diethylene glycol dimethyl ether, 1-ethoxy-2-propanol and ethyl lactate, in which the photoacid generator is most
5 soluble, and propylene glycol monomethyl ether acetate which is safe, and mixtures thereof.

[0076]

Suitable examples of the photoacid generator (C) include onium salts of general formula (18) below,
10 diazomethane derivatives of formula (19), glyoxime derivatives of formula (20), β -ketosulfone derivatives, disulfone derivatives, nitrobenzylsulfonate derivatives, sulfonic acid ester derivatives, and imidoyl sulfonate derivatives.

15



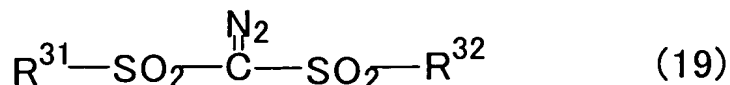
In the formula, R^{30} is a straight, branched or cyclic alkyl of 1 to 12 carbon atoms, an aryl of 6 to 12 carbon atoms, or
20 an aralkyl of 7 to 12 carbon atoms; M^+ is iodonium or sulfonium; K^- is a non-nucleophilic counter-ion; and the letter b is 2 or 3.

[0077]

Illustrative examples of alkyl groups represented by
25 R^{30} include methyl, ethyl, propyl, butyl, cyclohexyl, 2-oxocyclohexyl, norbornyl, and adamantyl. Exemplary aryl groups include phenyl; alkoxyphenyl groups such as p-methoxyphenyl, m-methoxyphenyl, o-methoxyphenyl, ethoxyphenyl, p-tert-butoxyphenyl, and m-tert-butoxyphenyl;
30 and alkylphenyl groups such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, ethylphenyl, 4-tert-butylphenyl, 4-butylphenyl, and dimethylphenyl. Exemplary aralkyl groups include benzyl and phenethyl. Examples of the non-nucleophilic counter-ion represented by
35 K^- include halide ions such as chloride and bromide; fluoroalkylsulfonate ions such as triflate, 1,1,1-trifluoroethanesulfonate, and nonafluorobutanesulfonate; arylsulfonate ions such as

tosylate, benzenesulfonate, 4-fluorobenzenesulfonate, and 1,2,3,4,5-pentafluorobenzenesulfonate; and alkylsulfonate ions such as mesylate and butanesulfonate.

[0078]



5

In the formula, R^{31} and R^{32} are straight, branched or cyclic alkyl or halogenated alkyl groups of 1 to 12 carbon atoms, aryl or halogenated aryl groups of 6 to 12 carbon atoms, or aralkyl groups of 7 to 12 carbon atoms.

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[0079]

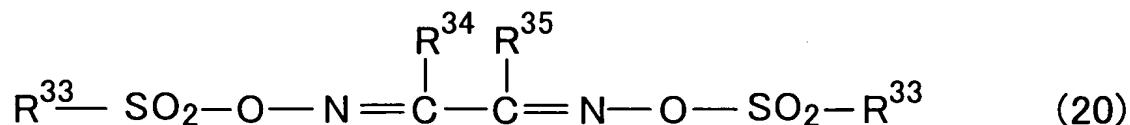
Illustrative examples of alkyl groups represented by R^{31} and R^{32} include methyl, ethyl, propyl, butyl, amyl, cyclopentyl, cyclohexyl, norbornyl, and adamantyl. Exemplary halogenated alkyl groups include trifluoromethyl, 1,1,1-trifluoroethyl, 1,1,1-trichloroethyl, and nonafluorobutyl. Exemplary aryl groups include phenyl; alkoxyphenyl groups such as p-methoxyphenyl, m-methoxyphenyl, o-methoxyphenyl, ethoxyphenyl, p-tert-butoxyphenyl, and m-tert-butoxyphenyl; and alkylphenyl groups such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, ethylphenyl, 4-tert-butylphenyl, 4-butylphenyl, and dimethylphenyl. Exemplary halogenated aryl groups include fluorobenzene, chlorobenzene, and 1,2,3,4,5-pentafluorobenzene. Exemplary aralkyl groups include benzyl and phenethyl.

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[0080]



In the formula, R^{33} , R^{34} , and R^{35} are straight, branched or cyclic alkyl or halogenated alkyl groups of 1 to 12 carbon atoms, aryl or halogenated aryl groups of 6 to 12 carbon atoms, or aralkyl groups of 7 to 12 carbon atoms. R^{34} and R^{35}

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may together form a cyclic structure with the proviso that if they form a cyclic structure, each is a straight or branched alkylene group of 1 to 6 carbon atoms.

[0081]

5 The alkyl, halogenated alkyl, aryl, halogenated aryl, and aralkyl groups represented by R^{33} , R^{34} , and R^{35} are exemplified by the same groups as mentioned above for R^{31} and R^{32} . Examples of alkylene groups represented by R^{34} and R^{35} include methylene, ethylene, propylene, butylene, and
10 hexylene.

[0082]

Illustrative examples of the photoacid generator include:

onium salts such as diphenyliodonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)phenyliodonium trifluoromethanesulfonate, diphenyliodonium p-toluenesulfonate, (p-tert-butoxyphenyl)phenyliodonium p-toluenesulfonate, triphenylsulfonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium trifluoromethanesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethanesulfonate, triphenylsulfonium p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium p-toluenesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium p-toluenesulfonate, tris(p-tert-butoxyphenyl)sulfonium p-toluenesulfonate, triphenylsulfonium nonafluorobutanesulfonate, triphenylsulfonium butanesulfonate, trimethylsulfonium trifluoromethanesulfonate, trimethylsulfonium p-toluenesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium p-toluenesulfonate, dimethylphenylsulfonium trifluoromethanesulfonate, dimethylphenylsulfonium p-toluenesulfonate, dicyclohexylphenylsulfonium trifluoromethanesulfonate, and dicyclohexylphenylsulfonium p-toluenesulfonate;

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diazomethane derivatives such as

bis(benzenesulfonyl)diazomethane,
bis(p-toluenesulfonyl)diazomethane,
bis(xylenesulfonyl)diazomethane,
5 bis(cyclohexylsulfonyl)diazomethane,
bis(cyclopentylsulfonyl)diazomethane,
bis(n-butylsulfonyl)diazomethane,
bis(isobutylsulfonyl)diazomethane,
bis(sec-butylsulfonyl)diazomethane,
10 bis(n-propylsulfonyl)diazomethane,
bis(isopropylsulfonyl)diazomethane,
bis(tert-butylsulfonyl)diazomethane,
bis(n-amylsulfonyl)diazomethane,
bis(isoamylsulfonyl)diazomethane,
15 bis(sec-amylsulfonyl)diazomethane,
bis(tert-amylsulfonyl)diazomethane,
1-cyclohexylsulfonyl-1-(tert-butylsulfonyl)diazomethane,
1-cyclohexylsulfonyl-1-(tert-amylsulfonyl)diazomethane, and
1-tert-amylsulfonyl-1-(tert-butylsulfonyl)diazomethane;

20 glyoxime derivatives such as

bis-o-(p-toluenesulfonyl)- α -dimethylglyoxime,
bis-o-(p-toluenesulfonyl)- α -diphenylglyoxime,
bis-o-(p-toluenesulfonyl)- α -dicyclohexylglyoxime,
bis-o-(p-toluenesulfonyl)-2,3-pentanedione-glyoxime,
25 bis-o-(p-toluenesulfonyl)-2-methyl-3,4-pentanedione-glyoxime,
bis-o-(n-butanesulfonyl)- α -dimethylglyoxime,
bis-o-(n-butanesulfonyl)- α -diphenylglyoxime,
bis-o-(n-butanesulfonyl)- α -dicyclohexylglyoxime,
bis-o-(n-butanesulfonyl)-2,3-pentanedione-glyoxime,
30 bis-o-(n-butanesulfonyl)-2-methyl-3,4-pentanedione-glyoxime,
bis-o-(methanesulfonyl)- α -dimethylglyoxime,
bis-o-(trifluoromethanesulfonyl)- α -dimethylglyoxime,
bis-o-(1,1,1-trifluoroethanesulfonyl)- α -dimethylglyoxime,
bis-o-(tert-butanesulfonyl)- α -dimethylglyoxime,

bis-o-(perfluorooctanesulfonyl)- α -dimethylglyoxime,
bis-o-(cyclohexanesulfonyl)- α -dimethylglyoxime,
bis-o-(benzenesulfonyl)- α -dimethylglyoxime,
bis-o-(p-fluorobenzenesulfonyl)- α -dimethylglyoxime,
5 bis-o-(p-tert-butylbenzenesulfonyl)- α -dimethylglyoxime,
bis-o-(xylenesulfonyl)- α -dimethylglyoxime, and
bis-o-(camphorsulfonyl)- α -dimethylglyoxime;

β -ketosulfone derivatives such as

2-cyclohexylcarbonyl-2-(p-toluenesulfonyl)propane and
10 2-isopropylcarbonyl-2-(p-toluenesulfonyl)propane;

disulfone derivatives such as diphenyl disulfone and
dicyclohexyl disulfone;

nitrobenzyl sulfonate derivatives such as

2,6-dinitrobenzyl p-toluenesulfonate and 2,4-dinitrobenzyl
15 p-toluenesulfonate;

sulfonic acid ester derivatives such as

1,2,3-tris(methanesulfonyloxy)benzene,
1,2,3-tris(trifluoromethanesulfonyloxy)benzene, and
1,2,3-tris(p-toluenesulfonyloxy)benzene; and

20 imidoyl sulfonate derivatives such as
phthalimidoyl triflate, phthalimidoyl tosylate,
5-norbornene-2,3-dicarboxyimidoyl triflate,
5-norbornene-2,3-dicarboxyimidoyl tosylate, and
5-norbornene-2,3-dicarboxyimidoyl n-butylsulfonate.

25 Preferred among these photoacid generators are onium
salts such as triphenylsulfonium trifluoromethanesulfonate,
(p-tert-butoxyphenyl)diphenylsulfonium trifluoromethane-
sulfonate, tris(p-tert-butoxyphenyl)sulfonium
trifluoromethanesulfonate, triphenylsulfonium
30 p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium
p-toluenesulfonate, and tris(p-tert-butoxyphenyl)sulfonium
p-toluenesulfonate; diazomethane derivatives such as
bis(benzenesulfonyl)diazomethane,
bis(p-toluenesulfonyl)diazomethane,
35 bis(cyclohexylsulfonyl)diazomethane,

bis(n-butylsulfonyl)diazomethane,
bis(isobutylsulfonyl)diazomethane,
bis(sec-butylsulfonyl)diazomethane,
bis(n-propylsulfonyl)diazomethane,
5 bis(isopropylsulfonyl)diazomethane, and
bis(tert-butylsulfonyl)diazomethane; and
glyoxime derivatives such as bis-o-(p-toluenesulfonyl)- α -
dimethylglyoxime and bis-o-(n-butan sulfonyl)- α -
dimethylglyoxime. These photoacid generators may be used
10 singly or in combinations of two or more thereof. Onium
salts are effective for improving rectangularity, while
diazomethane derivatives and glyoxime derivatives are
effective for reducing standing waves. The combination of
an onium salt with a diazomethane or a glyoxime derivative
15 allows for fine adjustment of the profile.

[0083]

The photoacid generator is preferably added in an
amount of 0.2 to 15 parts by weight, and especially 0.5 to 8
parts by weight, per 100 parts by weight of the base resin.
20 At less than 0.2 part, the amount of acid generated during
exposure would be too small and the sensitivity and
resolution be poor, whereas the addition of more than 15
parts would lower the transmittance of the resist and result
in a poor resolution.

25 [0084]

The basic compound is preferably a compound capable of
suppressing the rate of diffusion when the acid generated by
the photoacid generator diffuses within the resist film.
The inclusion of this type of basic compound holds down the
30 rate of acid diffusion within the resist film, resulting in
better resolution. In addition, it suppresses changes in
sensitivity following exposure, thus reducing substrate and
environment dependence, as well as improving the exposure
latitude and the pattern profile. (See JP-A 5-232706,
35 5-249683, 5-158239, 5-249662, 5-257282, 5-289322, and
5-289340.)

[0085]

Examples of suitable basic compounds include primary, secondary, and tertiary aliphatic amines, mixed amines, aromatic amines, heterocyclic amines, carboxyl group-bearing
5 nitrogenous compounds, sulfonyl group-bearing nitrogenous compounds, hydroxyl group-bearing nitrogenous compounds, hydroxyphenyl group-bearing nitrogenous compounds, alcoholic nitrogenous compounds, amide derivatives, and imide derivatives. Of these, aliphatic amines are especially
10 preferred.

[0086]

Examples of suitable primary aliphatic amines include ammonia, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, iso-butylamine,
15 sec-butylamine, tert-butylamine, pentylamine, tert-amylamine, cyclopentylamine, hexylamine, cyclohexylamine, heptylamine, octylamine, nonylamine, decylamine, dodecylamine, cetylamine, methylenediamine, ethylenediamine, and tetraethylenepentamine. Examples of
20 suitable secondary aliphatic amines include dimethylamine, diethylamine, di-n-propylamine, di-iso-propylamine, di-n-butylamine, di-iso-butylamine, di-sec-butylamine, dipentylamine, dicyclopentylamine, dihexylamine, dicyclohexylamine, diheptylamine, dioctylamine,
25 dinonylamine, didecylamine, didodecylamine, dicetylamine, N,N-dimethylmethylenediamine, N,N-dimethylethylenediamine, and N,N-dimethyltetraethylenepentamine. Examples of suitable tertiary aliphatic amines include trimethylamine, triethylamine, tri-n-propylamine, tri-iso-propylamine,
30 tri-n-butylamine, tri-iso-butylamine, tri-sec-butylamine, tripentylamine, tricyclopentylamine, trihexylamine, tricyclohexylamine, triheptylamine, trioctylamine, trinonylamine, tridecylamine, tridodecylamine, tricetylamine, N,N,N',N'-tetramethylmethylenediamine,
35 N,N,N',N'-tetramethylethylenediamine, and N,N,N',N'-tetramethyltetraethylenepentamine.

[0087]

Examples of suitable mixed amines include dimethylethylamine, methylethylpropylamine, benzylamine, phenethylamine, and benzyldimethylamine. Examples of
5 suitable aromatic and heterocyclic amines include aniline derivatives (e.g., aniline, N-methylaniline, N-ethylaniline, N-propylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, ethylaniline, propylaniline, trimethylaniline, 2-nitroaniline,
10 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline, 2,6-dinitroaniline, 3,5-dinitroaniline, and N,N-dimethyltoluidine), diphenyl(p-tolyl)amine, methyldiphenylamine, triphenylamine, phenylenediamine, naphthylamine, diaminonaphthalene, pyrrole derivatives
15 (e.g., pyrrole, 2H-pyrrole, 1-methylpyrrole, 2,4-dimethylpyrrole, 2,5-dimethylpyrrole, and N-methylpyrrole), oxazole derivatives (e.g., oxazole and isooxazole), thiazole derivatives (e.g., thiazole and isothiazole), imidazole derivatives (e.g., imidazole,
20 4-methylimidazole, and 4-methyl-2-phenylimidazole), pyrazole derivatives, furazan derivatives, pyrroline derivatives (e.g., pyrroline and 2-methyl-1-pyrroline), pyrrolidine derivatives (e.g., pyrrolidine, N-methylpyrrolidine, pyrrolidinone, and N-methylpyrrolidone), imidazoline
25 derivatives, imidazolidine derivatives, pyridine derivatives (e.g., pyridine, methylpyridine, ethylpyridine, propylpyridine, butylpyridine, 4-(1-butylpentyl)pyridine, dimethylpyridine, trimethylpyridine, triethylpyridine, phenylpyridine, 3-methyl-2-phenylpyridine,
30 4-tert-butylpyridine, diphenylpyridine, benzylpyridine, methoxypyridine, butoxypyridine, dimethoxypyridine, 1-methyl-2-pyridine, 4-pyrrolidinopyridine, 1-methyl-4-phenylpyridine, 2-(1-ethylpropyl)pyridine, aminopyridine, and dimethylaminopyridine), pyridazine
35 derivatives, pyrimidine derivatives, pyrazine derivatives, pyrazoline derivatives, pyrazolidine derivatives, piperidine derivatives, piperazine derivatives, morpholine derivatives,

indole derivatives, isoindole derivatives, 1H-indazole derivatives, indoline derivatives, quinoline derivatives (e.g., quinoline and 3-quinolinecarbonitrile), isoquinoline derivatives, cinnoline derivatives, quinazoline derivatives, 5 quinoxaline derivatives, phthalazine derivatives, purine derivatives, pteridine derivatives, carbazole derivatives, phenanthridine derivatives, acridine derivatives, phenazine derivatives, 1,10-phenanthroline derivatives, adenine derivatives, adenosine derivatives, guanine derivatives, 10 guanosine derivatives, uracil derivatives, and uridine derivatives.

[0088]

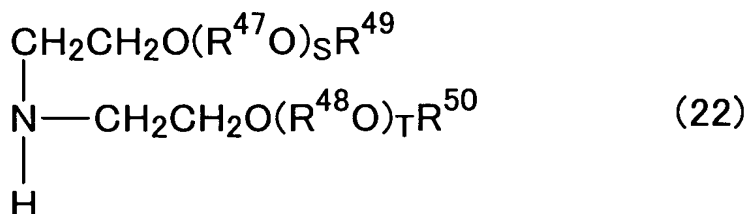
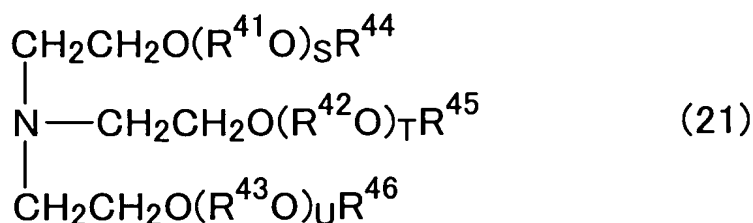
Examples of suitable carboxyl group-bearing nitrogenous compounds include aminobenzoic acid, 15 indolecarboxylic acid, and amino acid derivatives (e.g. nicotinic acid, alanine, alginine, aspartic acid, glutamic acid, glycine, histidine, isoleucine, glycyllleucine, leucine, methionine, phenylalanine, threonine, lysine, 3-aminopyrazine-2-carboxylic acid, and methoxyalanine). 20 Examples of suitable sulfonyl group-bearing nitrogenous compounds include 3-pyridinesulfonic acid and pyridinium p-toluenesulfonate. Examples of suitable hydroxyl group-bearing nitrogenous compounds, hydroxyphenyl group-bearing nitrogenous compounds, and alcoholic 25 nitrogenous compounds include 2-hydroxypyridine, aminocresol, 2,4-quinolinediol, 3-indolemethanol hydrate, monoethanolamine, diethanolamine, triethanolamine, N-ethyldiethanolamine, N,N-diethylethanolamine, triisopropanolamine, 2,2'-iminodiethanol, 2-aminoethanol, 30 3-amino-1-propanol, 4-amino-1-butanol, 4-(2-hydroxyethyl)morpholine, 2-(2-hydroxyethyl)pyridine, 1-(2-hydroxyethyl)piperazine, 1-[2-(2-hydroxyethoxy)ethyl]-piperazine, piperidine ethanol, 1-(2-hydroxyethyl)-pyrrolidine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 35 3-piperidino-1,2-propanediol, 3-pyrrolidino-1,2-propanediol, 8-hydroxyjulolidine, 3-quinuclidinol, 3-tropanol, 1-methyl-2-pyrrolidine ethanol, 1-aziridine ethanol,

N-(2-hydroxyethyl)phthalimide, and N-(2-hydroxyethyl)-isonicotinamide. Examples of suitable amide derivatives include formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, and benzamide. Suitable imide derivatives

[0089]

In addition, basic compounds of the following general formulas (21) and (22) may also be included.

[0090]



In the formulas, R^{41} , R^{42} , R^{43} , R^{47} and R^{48} are independently straight, branched or cyclic alkyls of 1 to 20 carbon atoms; R^{44} , R^{45} , R^{46} , R^{49} and R^{50} are hydrogen, alkyls of 1 to 20 carbon atoms, or amino; R^{44} and R^{45} , R^{45} and R^{46} , R^{44} and R^{46} , R^{44} with R^{45} and R^{46} , and R^{49} and R^{50} may bond together to form rings; and S, T and U are each integers from 0 to 20, with the proviso that hydrogen is excluded from R^{44} , R^{45} , R^{46} , R^{49} and R^{50} when S, T and U are equal to 0.

[0091]

The alkylene groups represented by R^{41} , R^{42} , R^{43} , R^{47} and R^{48} preferably have 1 to 20 carbon atoms, more preferably 1 to 10 carbon atoms, and most preferably 1 to 8 carbon atoms. Examples include methylene, ethylene, n-propylene, isopropylene, n-butylene, isobutylene, n-pentylene,

isopentylene, hexylene, nonylene, decylene, cyclopentylene, and cyclohexylene.

[0092]

The alkyl groups represented by R^{44} , R^{45} , R^{46} , R^{49} and R^{50} preferably have 1 to 20 carbon atoms, more preferably 1 to 8 carbon atoms, and most preferably 1 to 6 carbon atoms, and may be straight, branched or cyclic. Examples include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, hexyl, nonyl, decyl, dodecyl, tridecyl, cyclopentyl, and cyclohexyl.

[0093]

Where R^{44} and R^{45} , R^{45} and R^{46} , R^{44} and R^{46} , R^{44} with R^{45} and R^{46} , and R^{49} and R^{50} form rings, the rings preferably have 1 to 20 carbon atoms, more preferably 1 to 8 carbon atoms, and most preferably 1 to 6 carbon atoms, and may have branching alkyl groups of 1 to 6 carbon atoms, and especially 1 to 4 carbon atoms.

[0094]

S, T, and U are each integers from 0 to 20, preferably from 1 to 10, and more preferably from 1 to 8.

[0095]

Illustrative examples of the compounds of formulas (21) and (22) include tris{2-(methoxymethoxy)ethyl}amine, tris{2-(methoxyethoxy)ethyl}amine, tris[2-((2-methoxyethoxy)methoxy)ethyl]amine, tris{2-(2-methoxyethoxy)-ethyl}amine, tris{2-(1-methoxyethoxy)ethyl}amine, tris{2-(1-ethoxyethoxy)ethyl}amine, tris{2-(1-ethoxypropoxy)-ethyl}amine, tris[2-((2-hydroxyethoxy)ethoxy)ethyl]amine, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane, 1,4,10,13-tetraoxa-7,16-diazabicyclooctadecane, 1-aza-12-crown-4, 1-aza-15-crown-5, and 1-aza-18-crown-6. Especially preferred basic compounds are tertiary amines, aniline derivatives, pyrrolidine derivatives, pyridine derivatives, quinoline derivatives, amino acid derivatives, hydroxyl group-bearing nitrogenous compounds, hydroxyphenyl group-bearing nitrogenous compounds, alcoholic nitrogenous

compounds, amide derivatives, imide derivatives, tris{2-(methoxymethoxy)ethyl}amine, tris{2-(2-methoxyethoxy)-ethyl}amine, tris[2-((2-methoxyethoxy)methyl)ethyl]amine, and 1-aza-15-crown-5.

5 [0096]

The above-described basic compound may be used singly or in combinations of two or more thereof, and is preferably formulated in an amount of 0.01 to 2 parts, and especially 0.01 to 1 part by weight, per 100 parts by weight of the
10 base resin. At less than 0.01 part, the desired effects of the basic compound would not be apparent, while the use of more than 2 parts would result in too low a sensitivity.

[0097]

The dissolution inhibitor is a compound with a
15 molecular weight of up to 3,000 which changes its solubility in an alkaline developer under the action of an acid. Typically, a compound obtained by partially or entirely substituting acid labile substituents on a phenol or carboxylic acid derivative having a molecular weight of up
20 to 2,500 is added as the dissolution inhibitor.

[0098]

Examples of the phenol or carboxylic acid derivative having a molecular weight of up to 2,500 include 4,4'-(1-methylethylidene)bisphenol, (1,1'-biphenyl-4,4'-diol)-2,2'-
25 methylenebis(4-methylphenol), 4,4-bis(4'-hydroxyphenyl)-valeric acid, tris(4-hydroxyphenyl)methane, 1,1,1-tris(4'-hydroxyphenyl)ethane, 1,1,2-tris(4'-hydroxyphenyl)ethane, phenolphthalein, thimolphthalein, 3,3'-difluoro[(1,1'-biphenyl)-4,4'-diol], 3,3',5,5'-tetrafluoro[(1,1'-biphenyl)-
30 4,4'-diol], 4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]bisphenol, 4,4'-methylenebis(2-fluorophenol), 2,2'-methylenebis(4-fluorophenol), 4,4'-isopropylidenebis(2-fluorophenol), cyclohexylidenebis(2-fluorophenol), 4,4'-[(4-fluorophenyl)methylene]bis(2-fluorophenol), 4,4'-methylene-
35 bis(2,6-difluorophenol), 4,4'-(4-fluorophenyl)methylenebis(2,6-difluorophenol), 2,6-bis[(2-hydroxy-5-fluorophenyl)-methyl]-4-fluorophenol, 2,6-bis[(4-hydroxy-3-fluorophenyl)-

methyl]-4-fluorophenol, and 2,4-bis[(3-hydroxy-4-hydroxy-phenyl)methyl]-6-methylphenol. The acid labile substituents are the same as illustrated above for R¹³.

[0099]

5 Illustrative, non-limiting, examples of the dissolution inhibitors which are useful herein include 3,3',5,5'-tetrafluoro[(1,1'-biphenyl)-4,4'-di-t-butoxycarbonyl], 4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]bisphenol-4,4'-di-t-butoxycarbonyl,
10 bis(4-(2'-tetrahydropyranyloxy)phenyl)methane, bis(4-(2'-tetrahydrofuranyloxy)phenyl)methane, bis(4-tert-butoxyphenyl)methane, bis(4-tert-butoxycarbonyloxyphenyl)methane, bis(4-tert-butoxycarbonylmethyloxyphenyl)methane,
15 bis(4-(1'-ethoxyethoxy)phenyl)methane, bis(4-(1'-ethoxypropyloxy)phenyl)methane, 2,2-bis(4'-(2"-tetrahydropyranyloxy))propane, 2,2-bis(4'-(2"-tetrahydrofuranyloxy)phenyl)propane, 2,2-bis(4'-tert-butoxyphenyl)propane,
20 2,2-bis(4'-tert-butoxycarbonyloxyphenyl)propane, 2,2-bis(4-tert-butoxycarbonylmethyloxyphenyl)propane, 2,2-bis(4'-(1"-ethoxyethoxy)phenyl)propane, 2,2-bis(4'-(1"-ethoxypropyloxy)phenyl)propane, tert-butyl 4,4-bis(4'-(2"-tetrahydropyranyloxy)phenyl)-
25 valerate, tert-butyl 4,4-bis(4'-(2"-tetrahydrofuranyloxy)phenyl)-valerate, tert-butyl 4,4-bis(4'-tert-butoxyphenyl)valerate, tert-butyl 4,4-bis(4-tert-butoxycarbonyloxyphenyl)valerate, tert-butyl 4,4-bis(4'-tert-butoxycarbonylmethyloxyphenyl)-
30 valerate, tert-butyl 4,4-bis(4'-(1"-ethoxyethoxy)phenyl)valerate, tert-butyl 4,4-bis(4'-(1"-ethoxypropyloxy)phenyl)valerate, tris(4-(2'-tetrahydropyranyloxy)phenyl)methane, tris(4-(2'-tetrahydrofuranyloxy)phenyl)methane,
35 tris(4-tert-butoxyphenyl)methane, tris(4-tert-butoxycarbonyloxyphenyl)methane, tris(4-tert-butoxycarbonyloxymethylphenyl)methane,

tris(4-(1'-ethoxyethoxy)phenyl)methane,
tris(4-(1'-ethoxypropyloxy)phenyl)methane,
1,1,2-tris(4'-(2"-tetrahydropyranyloxy)phenyl)ethane,
1,1,2-tris(4'-(2"-tetrahydrofuranyloxy)phenyl)ethane,
5 1,1,2-tris(4'-tert-butoxyphenyl)ethane,
1,1,2-tris(4'-tert-butoxycarbonyloxyphenyl)ethane,
1,1,2-tris(4'-tert-butoxycarbonylmethyloxyphenyl)ethane,
1,1,2-tris(4'-(1'-ethoxyethoxy)phenyl)ethane,
1,1,2-tris(4'-(1'-ethoxypropyloxy)phenyl)ethane,
10 t-butyl 2-trifluoromethylbenzenecarboxylate,
t-butyl 2-trifluoromethylcyclohexanecarboxylate,
t-butyl decahydronaphthalene-2,6-dicarboxylate,
t-butyl cholate, t-butyl deoxycholate,
t-butyl adamantanecarboxylate, t-butyl adamantaneacetate,
15 and tetra-t-butyl 1,1'-bicyclohexyl-3,3',4,4'-
tetracarboxylate.

[0100]

In the resist composition according to the invention,
an appropriate amount of the dissolution inhibitor is up to
20 20 parts, and especially up to 15 parts by weight per 100
parts by weight of the base resin in the composition. With
more than 20 parts of the dissolution inhibitor, the resist
composition becomes less heat resistant because of an
increased content of monomer components.

25 [0101]

The resist composition of the invention may include,
as an optional ingredient, a surfactant which is commonly
used for improving the coating characteristics. Optional
ingredients may be added in conventional amounts so long as
30 this does not compromise the objects of the invention.

[0102]

A nonionic surfactant is preferred, examples of which
include perfluoroalkyl polyoxyethylene ethanols, fluorinated
alkyl esters, perfluoroalkylamine oxides, and fluorinated
35 organosiloxane compounds. Illustrative examples include
Florade FC-430 and FC-431 from Sumitomo 3M Ltd., Surflon
S-141, S-145, S-381 and S-383 from Asahi Glass Co., Ltd.,

Unidyne DS-401, DS-403, and DS-451 from Daikin Industries Ltd., Megaface F-8151, F-171, F-172, F-173 and F-177 from Dainippon Ink & Chemicals, Inc., and X-70-092 and X-70-093 from Shin-Etsu Chemical Co., Ltd. Preferred surfactants
5 include Florade FC-430 from Sumitomo 3M Ltd. and X-70-093 from Shin-Etsu Chemical Co., Ltd.

[0103]

Pattern formation using the resist composition of the invention may be carried out by a known lithographic
10 technique. For example, the resist composition may be applied onto a substrate such as a silicon wafer by spin coating or the like to form a resist film having a thickness of 0.1 to 1.0 μm , which is then pre-baked on a hot plate at 60 to 200°C for 10 seconds to 10 minutes, and preferably at
15 80 to 150°C for 1/2 to 5 minutes. A patterning mask having the desired pattern may then be placed over the resist film, and the film exposed through the mask to an electron beam or to high-energy radiation such as deep-UV rays having a wavelength below 300 nm, an excimer laser, or x-rays in a
20 dose of about 1 to 200 mJ/cm^2 , and preferably about 10 to 100 mJ/cm^2 , then post-exposure baked (PEB) on a hot plate at 60 to 150°C for 10 seconds to 5 minutes, and preferably at 80 to 130°C for 1/2 to 3 minutes. Finally, development may be carried out using as the developer an aqueous alkali
25 solution, such as 0.1 to 5%, and preferably 2 to 3%, tetramethylammonium hydroxide (TMAH), this being done by a conventional method such as dipping, puddling, or spraying for a period of 10 seconds to 3 minutes, and preferably 30 seconds to 2 minutes. These steps result in the formation
30 of the desired pattern on the substrate. Of the various types of high-energy radiation that may be used, the resist composition of the invention is best suited to micro-pattern formation with, in particular, deep-UV rays having a wavelength of 254 to 120 nm, an excimer laser, especially
35 ArF excimer laser (193 nm), F₂ excimer laser (157 nm), Kr₂ excimer laser (146 nm), KrAr excimer laser (134 nm) or Ar₂ excimer laser (126 nm), x-rays, or an electron beam. The

desired pattern may not be obtainable outside the upper and lower limits of the above range.

[0104]

[Effect of the Invention]

5 The resist composition comprising the polymer of the invention is sensitive to high-energy radiation, has excellent sensitivity and resolution at a wavelength of less than 200 nm, especially less than 170 nm, and excellent plasma etching resistance. Because these features of the
10 inventive resist composition enable its use particularly as a resist having a low absorption at the exposure wavelength of a F₂ excimer laser, a finely defined pattern having sidewalls perpendicular to the substrate can easily be formed, making the resist ideal as a micropatterning
15 material in VLSI fabrication.

[0105]

[EXAMPLE]

 Synthesis Examples and Examples of the invention are given below by way of illustration and not by way of
20 limitation.

[0106]

[Synthesis Example 1] Synthesis of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate

 A 500-ml three-necked flask was charged with 62.0 g of
25 cyclopentadiene resulting from pyrolysis of dicyclopentadiene. While the flask was placed in a water bath to keep the reaction temperature below 25°C, 125.6 g of 2,2,2-trifluoroethyl acrylate was added dropwise. The water bath was removed at the end of dropwise addition, and
30 stirring was continued overnight. The resulting oily substance was distilled in vacuum, collecting 147.2 g of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate. The yield was 82.0%.

[0107]

[Synthesis Example 2] Synthesis of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate

In a 1-liter four-necked flask, 75.3 g of
5 1-ethylcyclopentanol was dissolved in 300 g of methylene chloride. While the flask was placed in an ice bath, 65.7 g of acrylic chloride and a spoonful of dimethylaminopyridine were admitted into the flask. While the reaction temperature was kept below 15°C, 113.4 g of triethylamine
10 was added dropwise. The ice bath was removed at the end of dropwise addition, and stirring was continued for 3 hours, followed by ordinary post-treatment. The resulting oily substance was distilled in vacuum, collecting 86.8 g of 1-ethylcyclopentyl acrylate. The yield was 78.2%.

15 [0108]

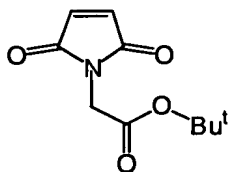
Next, using 85.0 g of 1-ethylcyclopentyl acrylate, reaction was carried out as in Synthesis Example 1. There was obtained 89.2 g of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate. The yield was
20 75.3%.

[0109]

[Synthesis Example 3] Synthesis of Monomer 1

A 1-liter three-necked flask was charged with 22.5 g of sodium hydride, and 350 g of dimethylformamide was
25 admitted thereto. While the flask was placed in an ice bath to keep the reaction temperature below 0°C, 75.7 g of maleimide was added dropwise. The ice bath was removed at the end of dropwise addition, and the reaction solution was ripened for 2 hours. While the flask was placed in a water
30 bath to keep the reaction temperature below 15°C, 123.3 g of tert-butyl chloroacetate was added dropwise. The water bath was removed at the end of dropwise addition, and stirring was continued for 3 hours, followed by ordinary post-treatment. The resulting oily substance was distilled
35 in vacuum, collecting 134.2 g of Monomer 1 shown below. The yield was 81.5%.

[0110]



Monomer 1

[0111]

[Synthesis Example 4] Ternary copolymerization reaction
5 of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-
carboxylate, 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-
carboxylate, and maleic anhydride

A 1-liter flask was charged with 75 g of
2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate,
10 80 g of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-
carboxylate, 67 g of maleic anhydride and 43 g of dioxane as
a solvent. The reactor was cooled to -70°C in a nitrogen
atmosphere, following which vacuum evacuation and nitrogen
flow were repeated three times. The flask was warmed up to
15 room temperature whereupon 9.0 g of an initiator AIBN was
added. The flask was heated at 60°C, at which reaction was
effected for 15 hours. The reaction solution was poured
into 10 liters of isopropyl alcohol whereupon a white solid
precipitated. The solid was collected by filtration and
20 dried in vacuum at 60°C, obtaining 173.8 g of a white
polymer.

[0112]

The polymer was analyzed by ¹³C-NMR, ¹H-NMR and GPC,
with the following analytical results.

25 Copolymer composition

2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate
: 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate
: maleic anhydride = 25:25:50

Mw = 8,700

30 Molecular weight dispersity (Mw/Mn) = 1.63

[0113]

[Synthesis Example 5] Ternary copolymerization reaction of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate, 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate, and N-methylmaleimide

A 1-liter flask was charged with 77 g of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate, 85 g of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate, 70 g of N-methylmaleimide and 43 g of dioxane as a solvent. The reactor was cooled to -70°C in a nitrogen atmosphere, following which vacuum evacuation and nitrogen flow were repeated three times. The flask was warmed up to room temperature whereupon 8.4 g of an initiator AIBN was added. The flask was heated at 60°C, at which reaction was effected for 15 hours. The reaction solution was poured into 10 liters of isopropyl alcohol whereupon a white solid precipitated. The solid was collected by filtration and dried in vacuum at 60°C, obtaining 160.8 g of a white polymer.

[0114]

The polymer was analyzed by ¹³C-NMR, ¹H-NMR and GPC, with the following analytical results.

Copolymer composition

2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate : 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate : N-methylmaleimide = 25:25:50

Mw = 8,400

Molecular weight dispersity (Mw/Mn) = 1.59

[0115]

[Synthesis Example 6] Binary copolymerization reaction of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate and Monomer 1

A 1-liter flask was charged with 135.5 g of 2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate, 130.0 g of Monomer 1, and 74 g of dioxane as a solvent. The reactor was cooled to -70°C in a nitrogen atmosphere, following which vacuum evacuation and nitrogen flow were

repeated three times. The flask was warmed up to room temperature whereupon 8.1 g of an initiator AIBN was added. The flask was heated at 60°C, at which reaction was effected for 15 hours. The reaction solution was poured into 10
5 liters of isopropyl alcohol whereupon a white solid precipitated. The solid was collected by filtration and dried in vacuum at 60°C, obtaining 217.7 g of a white polymer.

[0116]

10 The polymer was analyzed by ¹³C-NMR, ¹H-NMR and GPC, with the following analytical results.

Copolymer composition

2,2,2-trifluoroethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate
: Monomer 1 = 50:50

15 Mw = 9,200

Molecular weight dispersity (Mw/Mn) = 1.53

[0117]

[Comparative Synthesis Example 1] Binary copolymerization reaction of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-
20 carboxylate and N-methylmaleimide

In a 500-ml flask, 25 g of 1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate and 22 g of N-methylmaleimide were dissolved in 120 ml of toluene. Oxygen was thoroughly removed from the system, following
25 which 0.66 g of an initiator AIBN was added. The flask was heated at 60°C, at which polymerization reaction was effected for 24 hours. For purifying the resulting polymer, the reaction solution was poured into methanol whereupon the polymer precipitated. The procedure of dissolving the
30 collected polymer in acetone and pouring into 5 liters of methanol for precipitation was repeated twice. The polymer was separated and dried.

Copolymer composition

1-ethylcyclopentyl bicyclo[2.2.1]hept-5-ene-2-carboxylate :
35 N-methylmaleimide = 50:50

Mw = 9,700

Molecular weight dispersity (Mw/Mn) = 1.63

[0118]

[Comparative Synthesis Example 2] Binary copolymerization reaction of ethyladamantane methacrylate and γ -butyrolactone methacrylate

5 In a 500-ml flask, 20 g of ethyladamantane methacrylate and 16 g of γ -butyrolactone methacrylate were dissolved in 120 ml of toluene. Oxygen was thoroughly removed from the system, following which 0.66 g of an initiator AIBN was added. The flask was heated at 60°C, at
10 which polymerization reaction was effected for 24 hours.

For purifying the resulting polymer, the reaction solution was poured into methanol whereupon the polymer precipitated. The procedure of dissolving the collected polymer in acetone and pouring into 5 liters of methanol for
15 precipitation was repeated twice. The polymer was separated and dried.

Copolymer composition

ethyladamantane methacrylate : γ -butyrolactone methacrylate =
50:50

20 $M_w = 10,300$

Molecular weight dispersity (M_w/M_n) = 1.73

[0119]

Next, each of the polymers, 1 g, was thoroughly dissolved in 10 g of propylene glycol monomethyl ether
25 acetate (PGMEA), and passed through a 0.2- μ m filter, obtaining a polymer solution.

A polymer, designated Comparative Polymer 3, was synthesized from a monodisperse polyhydroxystyrene having a molecular weight of 10,000 and a dispersity (M_w/M_n) of 1.10
30 by substituting tetrahydropyranyl groups for 30% of the hydroxyl groups. Comparative Polymer 4 was poly(methyl methacrylate) having a molecular weight of 15,000 and a dispersity of 1.7. Comparative Polymer 5 was a novolak polymer having a meta/para ratio of 40/60, a molecular
35 weight of 9,000 and a dispersity of 2.5.

[0120]

The polymer solution was spin coated onto a MgF_2 substrate and baked on a hot plate at 100°C for 90 seconds, forming a polymer layer of 300 nm thick on the MgF_2 substrate. Using a vacuum ultraviolet spectrometer (VUV200S by Nihon Bunko K.K.), the polymer layer was measured for transmittance at 248 nm, 193 nm and 157 nm. The results are shown in Table 1.

[0121]

Table 1

Polymer	Transmittance (%) at 248 nm	Transmittance (%) at 193 nm	Transmittance (%) at 157 nm
Synthesis Polymer 4	88	85	33
Synthesis Polymer 5	87	42	35
Synthesis Polymer 6	86	40	38
Comparative Synthesis Polymer 1	85	26	22
Comparative Synthesis Polymer 2	92	86	10
Comparative Polymer 3	85	1	3
Comparative Polymer 4	90	70	1
Comparative Polymer 5	70	1	6

[0122]

[Examples and Comparative Examples]

Resist solutions were prepared in a conventional manner by using the components shown below in amounts shown in Table 2.

Next, on silicon wafers, DUV-30 (Nissan Chemical K.K.) was coated to form films of 55 nm thick so that the reflectance to KrF light (248 nm) was reduced below 1%. On the coated substrates, the resist solutions were spin coated, then baked on a hot plate at 100°C for 90 seconds to give resist films having a thickness of 300 nm. The resist films were exposed to a line-and-space pattern through a chromium mask by means of an excimer laser stepper

(NSR-S202A, from Nikon Corporation; NA 0.6, σ 0.75, 2/3 zone illumination). Immediately after exposure, the resist films were baked at 110°C for 90 seconds and then developed for 60 seconds with a 2.38% aqueous solution of tetramethylammonium hydroxide, thereby giving positive patterns.

[0123]

The resulting resist patterns were evaluated as described below. The results are shown in Tables 2 to 4. Evaluation:

The exposure dose which provided a 1:1 resolution at the top and bottom of a 0.20- μ m line-and-space pattern was the optimum exposure dose (Eop). The minimum line width (μ m) of a line-and-space pattern which was ascertained separately at this dose was the resolution of a test resist. Dry etching tests were carried out on the wafer to which the resist solution was spin coated under two sets of conditions.

[0124]

(1) Etching test with CHF₃/CF₄ gas

Using a dry etching instrument TE-8500P (Tokyo Electron K.K.), the difference in resist film thickness before and after etching was determined. The surface roughness of the etched film was measured by AFM.

The etching conditions are given below.

chamber pressure	40.0 Pa
RF power	1300 W
gap	9 mm
CHF ₃ gas flow rate	0.03 L/min
CF ₄ gas flow rate	0.03 L/min
Ar gas flow rate	0.10 L/min
time	60 sec

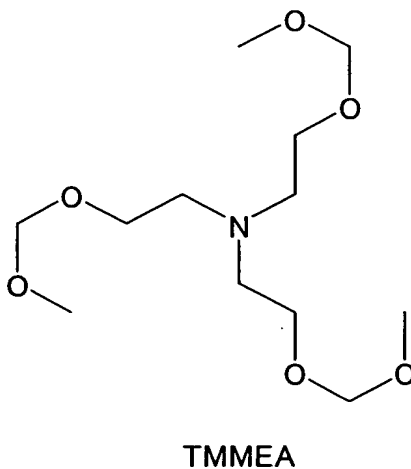
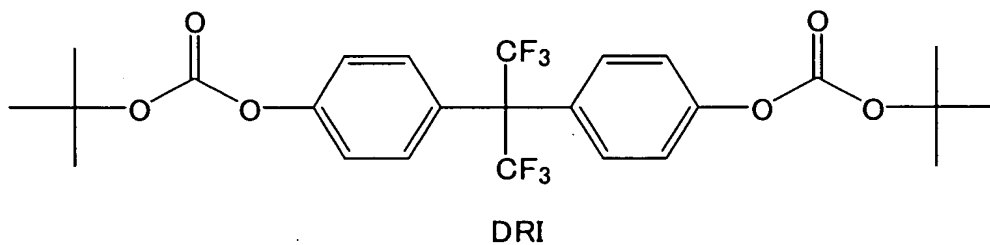
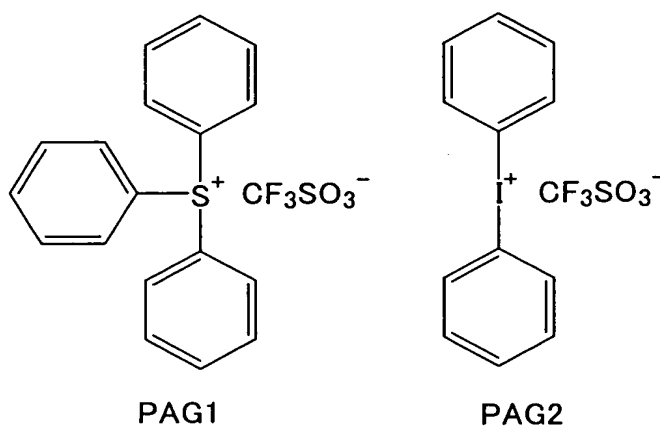
(2) Etching test with Cl₂/BCl₃ gas

Using a dry etching instrument L-507D-L (Nichiden Anerba K.K.), the difference in resist film thickness before and after etching was determined.

The etching conditions are given below.

	chamber pressure	40.0 Pa
	RF power	300 W
	gap	9 mm
	Cl ₂ gas flow rate	0.03 L/min
5	BCl ₃ gas flow rate	0.03 L/min
	CHF ₃ gas flow rate	0.10 L/min
	O ₂ gas flow rate	0.002 L/min
	time	360 sec

10 [0125]



[0126]

Table 2

Polymer (pbw)	Photoacid generator (pbw)	Basic compound (pbw)	Dissolution inhibitor/crosslinker (pbw)	Sensitivity (mJ/cm ²)	Resolution (μm)
Synthesis Example 4 (100)	PAG1 (2)	tributylamine (0.1)	-	40	0.18
Synthesis Example 5 (100)	PAG1 (2)	tributylamine (0.1)	-	40	0.18
Synthesis Example 6 (100)	PAG1 (2)	tributylamine (0.1)	-	32	0.17
Synthesis Example 6 (100)	PAG1 (2)	tributylamine (0.1)	DRI (20)	30	0.18
Synthesis Example 6 (100)	PAG2 (2)	tributylamine (0.1)	-	22	0.17
Synthesis Example 6 (100)	PAG1 (2)	triethanolamine (0.1)	-	38	0.17
Synthesis Example 6 (100)	PAG1 (2)	TMMEA (0.2)	-	40	0.17
Comparative Synthesis Example 1 (100)	PAG1 (2)	tributylamine (0.1)	-	45	0.18
Comparative Synthesis Example 2 (100)	PAG1 (2)	tributylamine (0.1)	-	25	0.16

[0127]

5

Table 3

Polymer	CHF ₃ /CF ₄ gas etching rate (nm/min)	Cl ₂ /BCl ₃ gas etching rate (nm/min)
Synthesis Polymer 4	99	120
Synthesis Polymer 5	95	122
Synthesis Polymer 6	98	128
Comparative Synthesis Polymer 1	97	122
Comparative Synthesis Polymer 2	90	105
Comparative Polymer 3	90	103
Comparative Polymer 4	180	350
Comparative Polymer 5	88	100

[0128]

Table 4

Polymer	Surface roughness Rms after CHF ₃ /CF ₄ gas etching (nm)
Synthesis Polymer 4	3.5
Synthesis Polymer 5	3.8
Synthesis Polymer 6	3.6
Comparative Synthesis Polymer 1	3.6
Comparative Synthesis Polymer 2	10.8
Comparative Polymer 3	2.2
Comparative Polymer 4	20.5
Comparative Polymer 5	1.5

5 [0129]

As is evident from Tables 1 to 4, resist materials using the polymers of the invention have sufficient transparency at the wavelength (157 nm) of F₂ excimer laser and satisfy the resolution and sensitivity requirements.

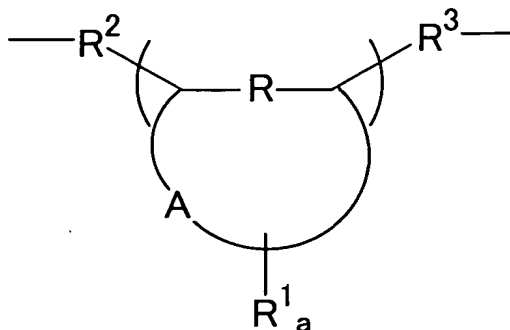
10 The difference in resist film thickness before and after etching is small and the surface roughness after etching is small enough, indicating superior dry etching resistance.

2000-127513

[ABSTRACT]

[Means for Solution]

A polymer comprising recurring units of the following general
5 formula (1):



(1)

wherein A is a divalent aliphatic or alicyclic hydrocarbon group
of 2 to 20 carbon atoms, R¹ is an alkyl group containing at least
one fluorine atom, which may contain a hetero atom such as oxygen,
10 nitrogen or sulfur to form an ether, ester, carbonate, alcohol,
acetoxo or thioester, "a" is a positive number of 1 to 3, and R,
R² and R³ each are a single bond or methylene group.

[Effect]

The resist composition comprising the polymer of the
15 invention is sensitive to high-energy radiation, has excellent
sensitivity and resolution at a wavelength of less than 200 nm,
especially less than 170 nm, and excellent plasma etching
resistance. Because these features of the inventive resist
composition enable its use particularly as a resist having a low
20 absorption at the exposure wavelength of a F₂ excimer laser, a
finely defined pattern having sidewalls perpendicular to the
substrate can easily be formed, making the resist ideal as a
micropatterning material in VLSI fabrication.

[Selected Drawing] none